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New methods of ambient air analysis were used to define more clearly the relationships between oxidants and their precursors. Non-methane hydrocarbons, NO_x, O_2, and oxidants were measured at the same time and location (Riverside, California). The ambient air data presented in this report are displayed as a series of conditional joint distributions. The correlations range from excellent--ozone vs oxidant--to poor or bimrodal--ozone with non-methane-ethane organics (NMEO) or with NO_x. The ratio of NMEO to NO_x was always higher than indicated by inventories and showed a large scatter. No depletion of NMEO with respect to acetylene could be detected.

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OXIDANT-PRECURSOR RELATIONSHIPS

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PREFACE

The air quality standard for ozone is exceeded by a wide margin on many days of the year and in many locations around the country. The inland area of Southern California is exceptionally vulnerable because it is downwind of the Los Angeles/Orange County megalopolis. Ozone, the most toxic component, can only be controlled by reducing emissions of its precursors. To establish standards for these precursors (hydrocarbons and nitrogen oxides), it is necessary to understand quantitatively the complex oxidant/precursor relationship as it controls the real ambient atmosphere. The project reported here was designed to provide "ground truth" data to support this effort and for comparison with laboratory or computer models of photochemical smog.

ABSTRACT

New methods of ambient air analysis were used to define more clearly the relationship between oxidant (ozone) and its precursors (hydrocarbons and nitrogen oxides). Nonmethane hydrocarbons (NMHC), nitrogen oxides, ozone, and oxidants were measured at the same time and location (Riverside, California). Such data are useful to establish the real world initial conditions for the interpretation of chamber data and as input for modeling studies.

An automated gas chromatograph was used for the direct measurement of organic compounds containing three or more carbon atoms along with methane and the three two-carbon hydrocarbons. Since the C_3^+ organics were measured by a backflush technique, the error-magnifying step of methane subtraction was avoided. Nitrogen oxides and nitric oxide were measured on the same samples so that meaningful ratios can be calculated. By adding the concentrations of ethene and acetylene to the concentration of C_3^+ organics values for nonmethane-ethane organic (NMEO) were obtained directly. The data in this project provide two separate methods for estimating extent of reaction. One is the ratio of nitric oxide to total nitrogen oxides. The other is the ratio of ethene to acetylene. Both decrease as the reaction proceeds.

The ambient air data were entered into punched cards and are displayed in this report as a series of conditional joint distributions. The correlations which appear range from excellent (ozone vs oxidant) to poor or bimodal (ozone with nonmethane ethane organics [NMEO] or with nitrogen oxides [NOx]). The ratio of NMEO to NOx was always higher than indicated by inventories but showed a large scatter. The ratio of ethene to acetylene in unreacted samples was about 1:1, the same as ten years ago. Samples which

were reacted as judged by ozone concentration showed depletion of ethene as compared to acetylene because of its greater reactivity. No depletion of NMEO with respect to acetylene could be detected.

Further development of the backflush technique for direct measurement of NMHC or NMEO is recommended along with development and exploitation of the conditional joint distribution analysis.

This report was submitted in fulfillment of grant No. R803799 by the Statewide Air Pollution Research Center, University of California, Riverside 92521 under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from July 21, 1975 to September 30, 1978 and work was completed September 30, 1978.

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ABREVIATIONS AND SYMBOLS

NMHC - non methane hydrocarbon

NMEO - non methane ethane organic

SCAB - South Coast Air Basin

CARB - California Air Resources Board

SCAQMD - South Coast Air Quality Management District

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SECTION 1

INTRODUCTION

Ozone is considered to be the major health hazard in photochemical smog and so control strategies have been directed toward reducing ozone exposures to acceptable levels. This toxic compound is a product of a very complex reaction of primary pollutants (hydrocarbons and nitric oxide) which are not themselves highly toxic. This means that control of ozone exposure depends on control of hydrocarbon and nitric oxide emissions. Emission standards must be stated quantitatively so it is necessary to develop a quantitative relationship between emissions of primary pollutants and subsequent ozone exposure. This has been a very difficult problem because the complexities of the photochemistry are compounded with those of meteorology, sunlight, and sources. In the actual event a non-methane hydrocarbon (NMHC) standard of 160 micrograms per cubic meter was established based on a review of ambient air data. Since hydrocarbon is a precursor of oxidant, the 6-9 AM average concentration was specified in the expectation that high hydrocarbon concentrations at this hour would lead to high ozone values later in the day.

The term "oxidant precursor" has quite a long history. It was first used to describe the fact that early morning air could be irradiated with artificial sunlight to produce oxidant. This experiment was done at the Stanford Research Institute and at that time (the mid-50s) there was no clue as to the nature of the precursor. Within a few years it became

evident that unirradiated morning air could be described as dilute auto exhaust even though it had none of the symptoms of photochemical smog. But irradiation of this "precursor" with artificial sunlight did produce oxidant. In later years, use was made of this ability of stable, early morning weather conditions to trap unreacted auto exhaust to study the nature of the hydrocarbon mix which was then present. Although this type of atmospheric stability will trap auto exhaust and other pollution in the early morning hours, it is not always followed by an afternoon of high photochemical smog because the radiation inversion responsible for early morning trapping (an example is shown in Figure 1) is destroyed by sunlight more rapidly than sunlight can convert exhaust into photochemical oxidant. In fact, one striking result was that in these early morning samples, even unreactive auto exhaust components such as acetylene were present in substantially higher concentrations than in afternoon samples in which smog was fully developed. In spite of the tenuous relationship between early morning concentrations of hydrocarbon and the oxidant history of the subsequent afternoon, the air quality standard for hydrocarbon was written in terms of the 6-9 AM concentrations of hydrocarbons (1). This was used not only to set the air quality standard for hydrocarbon but to estimate the degree of hydrocarbon control needed to attain the oxidant air quality standard. Both the needed degree of control and air quality standards can also be estimated using chamber irradiation data (2).

The new approach represented by this project was not meant to be a substitute for either chamber studies of oxidant formation in synthetic mixtures or for mathematical modeling of the photochemical reaction. It is instead designed to be a kind of "ground truth" measurement against which

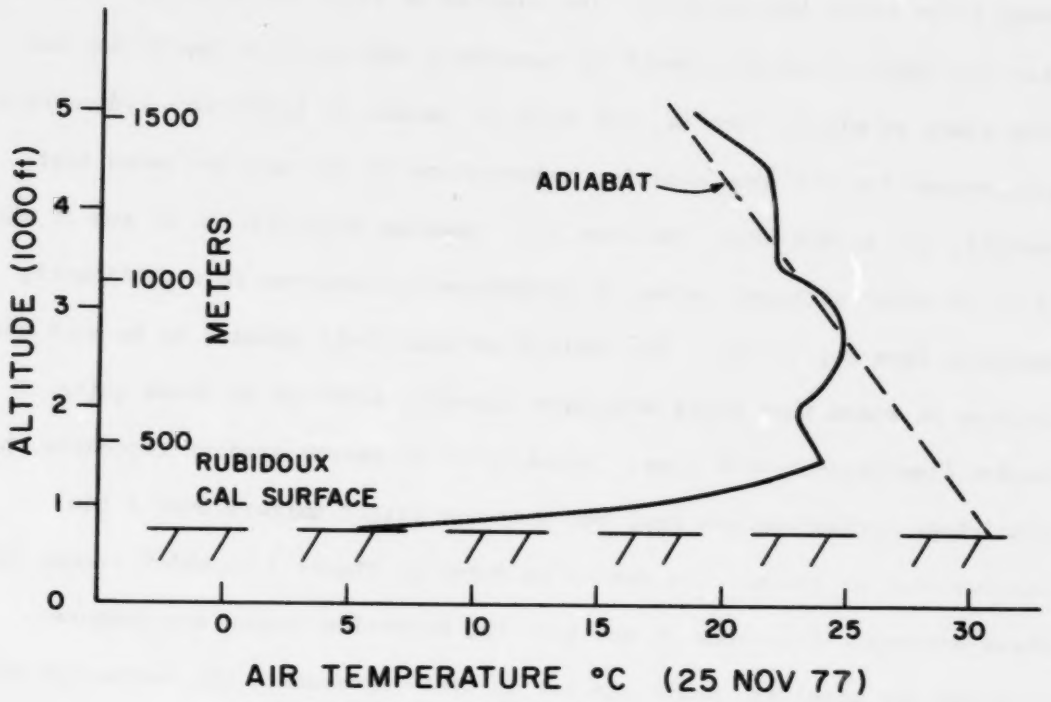

Figure 1. Surface radiation inversions like this (unusually shallow) one are almost always present near dawn. They concentrate pollutants emitted in the early hours in a very small volume, but are mixed when solar energy heats this small volume.

other methods of devising air qualtiy standards and control strategies can be compared. If all approaches could be reconciled to yield one strategy, we would be in a much stronger position to define and to defend that strategy. One unknown which can never be resolved by either chamber studies or modeling is the extent to which the mixture which is injected into a given atmosphere varies from day to day and from place to place. Sometimes it has been assumed that there are very wide variations in the hydrocarbon to NO_x ratio in the precursor mixture and even within in the hydrocarbon mix itself. Sound control strategy requires a knowledge as to whether this

needs to be taken into account. Our studies of light hydrocarbons indicate that the hydrocarbon mix itself is reasonably uniform from day to day and from place to place, that is, the relative amount of individual hydrocarbon are, except for the more reactive hydrocarbons or for samples taken near sources, are always about the same (3). Another objective is to see if the ratio of total nitrogen oxides to nonmethane hydrocarbon is significantly variable from day to day. The ambient oxidant field appears to be much more uniform in space than might have been thought, although it shows quite random fluctuations with time. Comparisons of nearby oxidant recorders show that these variations are real but they are fairly uniform over a few hundred feet of space. One record is shown in Figure 2 in which traces from three different locations on and near the Riverside campus are compared. Although the absolute levels are not in close agreement, the variations with time are remarkably similar.

The hydrocarbon standard was established with the aid of a plot of ambient air oxidant maxima against nonmethane hydrocarbon concentrations measured at 6-9 AM of the same day. An upper boundary drawn above this scatter pattern was taken to give the maximum oxidant which could be produced from this amount of hydrocarbon precursor (4). Such plots were used to set the hydrocarbon standard at a value required to meet the oxidant standard of 0.08 ppm (160 ug/m^3). They were also used to derive a % control diagram which became the "Appendix J" which was used to design control strategy (5). Although this approach had the merit of being based on actual polluted air data it could be and was criticized on a number of grounds. Perhaps the most serious is that the oxidant and its precursors are measured on different air parcels.

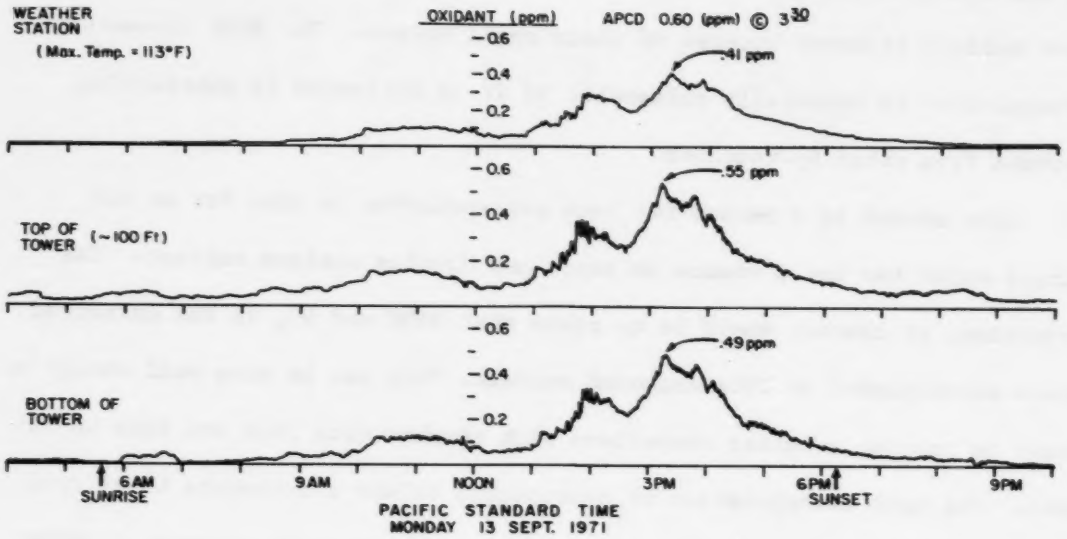

Figure 2. Three oxidant (KI) analyzers in different locations show the spatial uniformity of the oxidant field during a severe episode.

The various procedures used to estimate the degree of control required for auto emissions give answers varying between 90 and 97% or even more (6). While this may seem to be an acceptably narrow range, when translated into emissions standards it gives a variation in allowable emission of more than 3 to 1. This is far from trivial to the automotive engineer.

The assumption that the measured oxidant is produced by the measured early morning NMHC/NO_x is especially serious when the use to which these curves (scatter patterns) have been put is remembered. One draws a boundary

around the scatter pattern and extrapolates to the oxidant air quality standard. The position of the boundary is determined by those few points at the lowest values of NMHC and oxidant. These are also the points most subject to error because of their small values. The NMHC (nonmethane hydrocarbon) is especially vulnerable if it is estimated by subtracting methane from total hydrocarbon.

Also needed is a method for back extrapolation in time for an air parcel which has had a chance to react and develop maximum oxidant. The objective, of course, would be to state what NMHC and NO_x in the unreacted state corresponded to this measured oxidant. This can be done well enough at least to provide a better comparison with chamber data than the data so far used. For back extrapolation of hydrocarbon values a procedure first used in Reference (3) was adopted. In that paper the relative amounts of three hydrocarbons of widely differing reactivity (acetylene, ethene, and propene) were used to estimate that a Riverside smog had been photoreacted for six to eight hours. This estimate was then combined with data on photolysis of ambient air to estimate that about one-third of the NMHC had reacted. A fuller discussion is given in the appendix.

The chemiluminescent analyzer used for NO/NO_x analysis should automatically "back extrapolate" the NO_x concentration since the converter used to obtain the NO_x values reduces not only NO_2 but PAN and probably nitrate to NO (7). In the NO_x mode, the instrument therefore probably gives a good measure of the initial oxides of nitrogen. Catalytic reduction then constitutes back extrapolation.

In this program of data analysis much use is made of ratios of pollutants, partly because they are not affected by dilution and partly because

they reveal special characteristics of the air sample (for example, extent of photoreaction). A ratio of major importance is that of hydrocarbon (NMHC) to nitrogen oxides because of the use of oxidant isopleths derived from chamber experiments or modeling. Understanding of this relationship is vital to sound development of control strategy, air quality standards, and emission standards. Debate about emission standards will only end when "clean air" is achieved. Recent developments in ambient hydrocarbon analysis were exploited to provide a sounder data base for understanding the real atmospheric situation. Under EPA grant R803799 and after much difficulty, a backflush chromatograph was developed to measure hydrocarbon in ambient air. This instrument measures (separately) methane, ethane, ethene, acetylene and higher hydrocarbons on a single small sample of ambient air. This permits for the first time direct measurement of the widely discussed but infrequently measured nonmethane hydrocarbon (NMHC).

While dispersion models permit the estimation of ambient concentrations from source inventories they depend on parameters which are not usually known accurately. This makes comparison between ambient air quality and and emission inventory data of limited value. Ratios of pollutant concentrations are not affected by dilution so the emphasis in this project has been on comparison of ratios. It should be possible to reconcile at least approximately, the ratio of NMHC to NO_x found in the atmosphere with that estimated from emission inventories. Any gross discrepancy should be explored further. Since inventories are always stated in weight units to accommodate mixtures of unknown average molecular weight it is necessary to express ambient air concentrations the same way. By long custom, nitrogen oxides, NO_x, is expressed in weight units as though it were

all NO_2 even though combustion sources emit primarily NO. In this project, NO has been expressed by weight as NO; but NO_x has been expressed as NO_2 to facilitate comparison with emission inventories.

Table 1 shows inventories which have been published by various agencies for various areas in recent years. The weight ratio covers a range from 0.77 to 1.45 which is small considering that a number of years are covered and the lower figure is for cars only. It is also convenient to express hydrocarbon concentrations by weight since the flame ionization detector responds roughly according to weight and it can then be calibrated without regard to molecular weight.

TABLE 1. THE WEIGHT RATIO OF NMHC/NO_x.

Year	NMHC/NO_x	=	Ratio	Area	Agency	Ref.
	Tons/Day					
1972	$\frac{8.58 \times 10^4}{6.08 \times 10^4}$	=	1.41	USA	EPA	(8)
1973	$\frac{1760}{1210}$	=	1.45	SCAB*	CARB	(9)
1977	$\frac{1506.7}{1505.7}$	=	1.00	SCAB*	SCAQMD	(10)
	GM/MILE					
1977	$\frac{2.4}{3.1}$	=	0.77	Gasoline Vehicles	SCAQMD	(11)

*SCAB = South Coast Air Basin

This inventory ratio of about 1 may be compared with chamber data by reference to two papers in the "Internation Conference on Photochemical Oxidant Pollution and Its Control," EPA-600/3-77 001b, a meeting held in

September 1976. The paper by Dimitriades (#18.2, p. 871) describes "An alternative to the Appendix J method for calculating oxidant and NO_2 related control requirements." The following paper by Dodge (p. 881) explains the use of modeling techniques to supplement chamber data in development of this approach. The key concept is the use of the oxidant/O_3 isopleth diagram reproduced here (2).

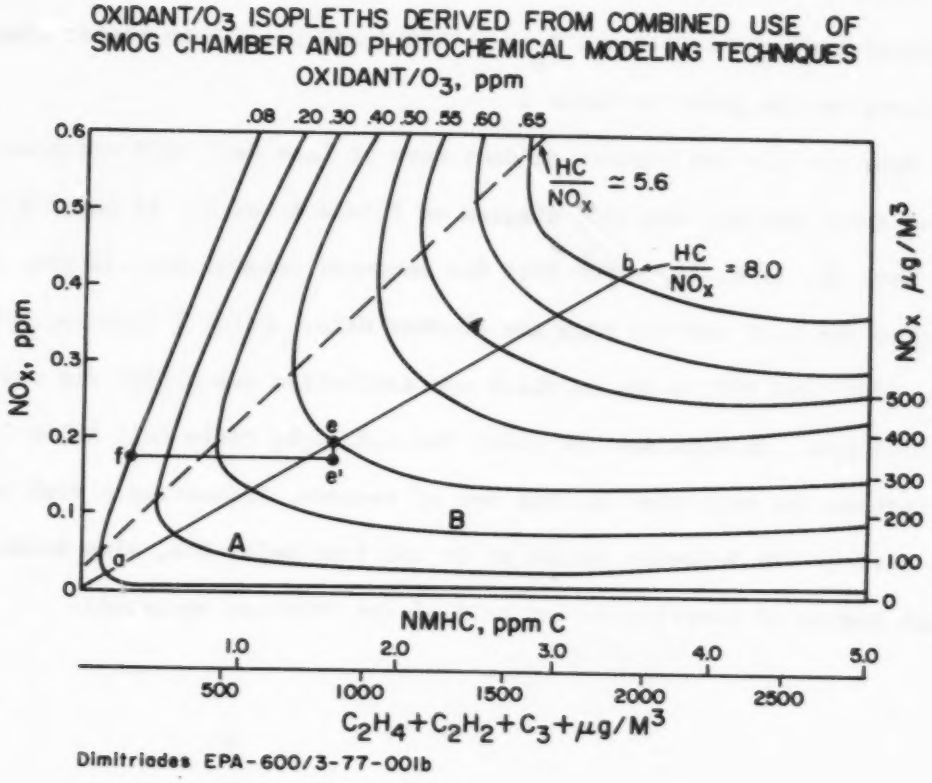

Figure 3. Diagram illustrating the oxidant isopleth strategy.

To bridge the gap to emission inventory data weight/m^3 scales have been added to this diagram (the two ratios given on the plot are by moles). To make use of this plot a data base of the NMHC and NO_x values in real polluted air is required. As stated in Dimitriades' paper, "The requisite data can be obtained through ambient measurements that must be sufficiently abundant to provide a reliable measure of the range of the NMHC-to-NO_x ratio." The NMHC/NO_x ratios of 5.6 and 8.0 given on the above plot must be multiplied by 14/46 = 0.304 for comparison with inventory weight ratios. The resulting values (1.7 and 2.43 gm NMHC/gmNO_x) are both higher than the inventory ratios given in Table 1.

Data for the two highest oxidant days of late fall 1976 are plotted on the above oxidant isopleth diagram as Points A and B. At point A (Saturday, Nov. 20, 1976, 1400-1600 PST) the measured oxidant was .18 ppm, very close to the 0.20 contour from the chamber data. Point B (Sunday, Nov. 21, 1976, 1600-1700 PST, a day on which eye irritation was noted) the oxidant was 0.21 ppm. On this day (at 1500) the C_2H_4/C_2H_2 ratio fell below 0.4 for perhaps the only time in this set of records, indicating a high degree of reaction. On Saturday (point A) it was just below 0.6, also indicating a high degree of reaction (about half of the ethylene consumed).

SECTION 2

CONCLUSIONS

The mass of data collected during this project was summarized in the form of joint distributions, some of which were conditional. This method of data study proved to be a useful way to analyze ambient air data. Some such distributions, which were expected to be highly correlated, are so; for example ozone/oxidant. Other distributions show greater scatter, which may be due in part to lack of precise time synchronization between different instruments.

The crucial non-methane ethane organic (NMEO) vs NO_x distributions show large spread, perhaps due in part to deficiencies in the time synchronization. This is true for all the conditions tested. The ratios of NMEO/NO_x are all several times larger than those suggested by emission inventories. This is true even for mixtures whose high nitric oxide content suggests that they were unreacted and for 6-9 am samples.

Non-methane ethane organic and acetylene are quite closely correlated and show no depletion to the former with high oxidant. Here there was no possible time synchronization error because the two quantities derive from the same sample and analyzer. The good correlation also suggests that these two components come from the same source (auto exhaust). Ethene and acetylene are also closely correlated for the same two reason. Components which come from different sources (for example acetylene and methane) show a lesser degree of correlation because they are similarly affected by

atmospheric stability.

The higher reactivity of the former hydrocarbon is reflected in a reduction of the ratio in those samples with high ozone. In unreacted samples the weight ratio was about 1:1 the same as it was ten years ago.

Joint distributions of ozone with NMEO and NO_x are bimodal reflecting the difference between reacted and unreacted samples. This is attributed more to meteorology than chemistry.

SECTION 3

RECOMMENDATIONS

The backflush gas chromatographic procedure should be further developed to provide better data on hydrocarbon pollution which excludes the naturally occurring and unreactive methane. This method avoids the subtraction step which magnifies errors. For maximum utility automated peak integration should be added to automated sampling.

Time synchronization of sampling should be carefully controlled to avoid data scatter where correlations, ratios or joint distributions are to be used in data reduction.

Concentration intervals should be carefully chosen in joint distribution analysis to avoid fictitious broadening of well correlated data. This method of analysis appears to have great potential for study of polluted air.

Concentrations should be expressed in weight units to facilitate comparison with inventory data.

Computer analysis using conditional joint distributions should be developed further as a method of study of polluted air.

SECTION 4

METHODS

UCR has maintained a weather station for many years in connection with its agricultural research. It is housed in a one room, air conditioned, cinder block building set in the middle of an agricultural field. This is a good sampling site since it is accessible, yet somewhat removed from heavy traffic. Air monitoring instruments have been operated in this house periodically for several years, the principle ones being a coulometric oxidant analyzer (Mast) and an automated PAN chromatograph. Oxidant levels correlate fairly well with those reported by state and country agencies in the area.

The air samples were taken from an existing installation in the weather station. The sample entered a 4" diameter aluminum irrigation pipe stack at a point about 30 ft above the ground. The sample pipe entered the building through the roof and was divided by a glass "T" into two 2" diameter glass pipes, 10′ and 15′ long respectively. Each glass pipe was vented to the roof to a 150 CFM blower. Table 2 summarizes the five instruments which were operated during this program.

One sample pipe supplied the PANanalyzer (electron capture gas chromatograph), oxidant analyzer and an ultraviolet ozone analyzer (Dasibi); the other supplied the NO-NO_x analyzer (TECO) and the hydrocarbon gas chromatograph. Each instrument obtained its sample through a 1/8" diameter Teflon tube.

Midway through the program (April 19, 1977), a 20-liter glass bottle was placed in the sample line to the NO-NO_x analyzer and the hydrocarbon chromatograph instruments. The flow through the bottle was provided by the NO-NO_x instrument sampling pump which pulls 50-56 /hr (1.8-2 SCF per hour)

TABLE 2. SUMMARY OF MEASUREMENTS (ALL ON A CONTINUOUS OR AUTOMATIC BASIS).

1.	Hydrocarbons - Gas chromatography with flame ionization. Direct injection measurement of methane, ethane, ethene, acetylene. Hydrocarbons of 3 or more carbons as one peak in back flush mode.
2.	Nitrogen Oxides - By ozone chemiluminescence. This measures NO and NO_x and the latter is taken to be total oxidized nitrogen.
3.	Ozone - By ultraviolet photometer. (Dasibi)
4.	Oxidant - By coulometric KI method. (Mast)
5.	UV Intensity - By recording UV meter. (Eppley)

thereby providing a 22-24 minute residence time for the sample in the bottle, as shown in Figure 4.

The hydrocarbon analysis reported in the previously cited reference (3) was carried out opportunistically, sporadically and manually. No paraffins higher than C_6 nor olefins higher than C_5 were measured. It was therefore necessary to estimate the higher molecular weight hydrocarbons. A new backflush chromatograph made it possible to monitor methane, the two-carbon hydrocarbons and C_3^+ hydrocarbons by automated direct sample injection followed by backflush. An eight-port valve automatically operated by a "valve minder" injected a 4.4-ml sample of ambient air.

Samples for the hydrocarbon chromatograph and PANanalyzer were taken at 15 minute intervals on the hour and quarter hour, using timers and solenoids which permitted unattended, around the clock operation.

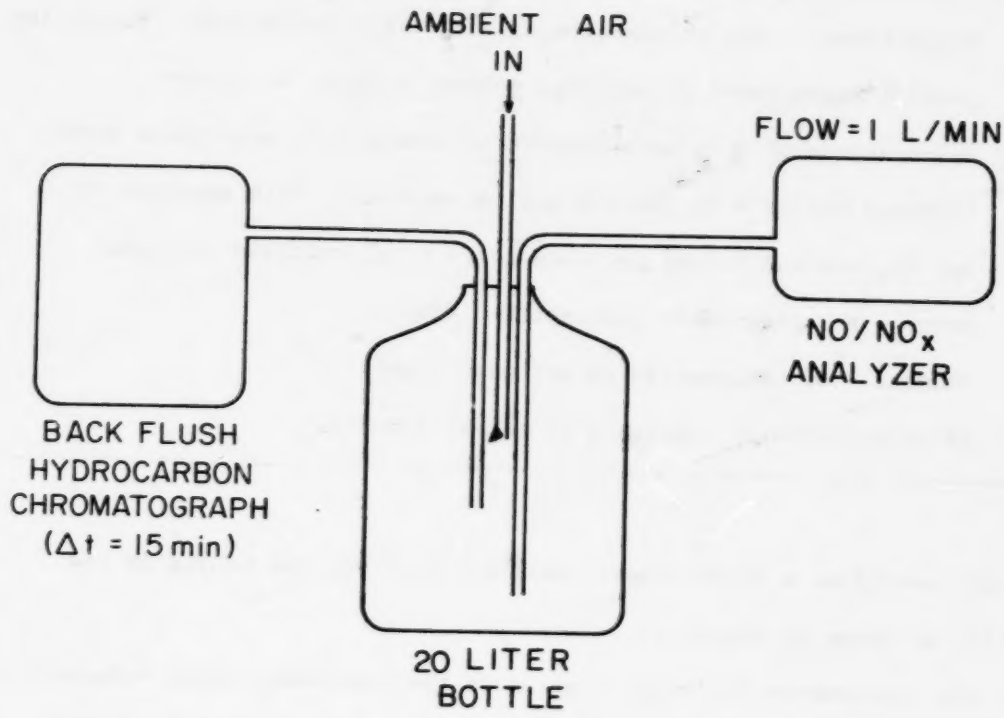

Figure 4. To insure comparability of hydrocarbon and NOx analytical data both instruments drew samples from a 20 liter intergrating bottle.

The analytical data were recorded first on strip charts since automation of the chromatographic output would be difficult. Data were then transferred to punch cards. Five hydrocarbon measurements with five other variables every 1/4 hour adds to 40 points per hour or 960 per day. This

made machine manipulation necessary. It also greatly facilitates grouping the data points according to ethene/acetylene ration (indicative of degree of reaction) or other variables.

HYDROCARBON ANALYSIS

"Conventional" methods of measuring NMHC rely on separate measurement of total hydrocarbon (THC) and methane followed by mathematical subtraction. The fact that methane, especially in relatively clean air, is a large part of the total makes this procedure vulnerable to the errors of subtracting two numbers which are both large compared to their difference. This procedure can produce apparent negative concentrations of NMHC if there are small errors in either THC or methane or if they are measured in separate samples. Negative values can clearly be rejected as spurious but their occurrence makes the accuracy of all positive values (especially the small values near the air quality standard) quite questionable. The background level of methane is about 1.38 ppmC and the air quality standard is 0.24 ppmC. An air sample containing exactly 0.24 ppmC of NMHC in addition to background methane would have a total of 1.62 ppmC. A small error in either the methane or total hydrocarbon measurement will produce a much larger percentage error in the NMHC. Any procedure which uses separate samples for the two measurements will be susceptible to such errors.

For these reasons it was decided to use a backflush technique for the measurement of higher hydrocarbons directly, rather than by difference, so that the same sample of air could be used for both. This represented a substantial extrapolation of prior techniques since freeze-out concentration could not be used with automated sampling and backflush. With the sample size thus restricted to 4.4 ml the peaks are small and noise and drift must

be kept to a minimum. Since the methane peak is much larger than the other four peaks it is recorded on the second channel of a two-pen recorder at a reduced sensitivity.

The principal problems encountered in setting up this method were in maintaining a flame in the detector and a stable baseline while reversing the column flow. The surge of carrier gas which accompanies reversal of flow snuffs the flame unless a buffer is inserted between the sampling valve and the flame detector.

The eight-port sample valve (Carle Model 2012) used in the configuration shown in Figure 5 provided direct analysis of methane, ethane, ethene, and acetylene. By using the backflush procedure the remainder of the hydrocarbons (C_3 and higher) were measured as a single peak. In the "sample and backflush" position the column was backflushed for 12 minutes, the sample loop was purged with sample air starting two minutes before the end of this period. In the last minute, the pump was turned off to allow the loop to equilibrate. In the "inject" position the contents of the sample loop were injected into the column to determine methane and the C_2 hydrocarbons in a three minute chromatogram.

Various restrictors were tried in the line between the valve and the flame detector to prevent flameout. These included a length of capillary tubing, tubing filled with Teflon beads, and various short columns containing Poropak N packing. Most successful was a 7.5 cm-long column filled with 50/80 Poropak N, which prevented flameout and provided the stable baseline needed for our operating conditions which were chosen to maximize instrument sensitivity.

For much of the program the instruments was plagued with a cyclic

drift often superimposed on another cyclic drift having a different time interval, and a random drift pattern affecting the baseline. The first cyclic drift, up on analysis, down on backflush, was thought to be caused by differences in flow which were not measureable. Elimination of the problem was attempted by shortening all capillary lines to the sample valve to

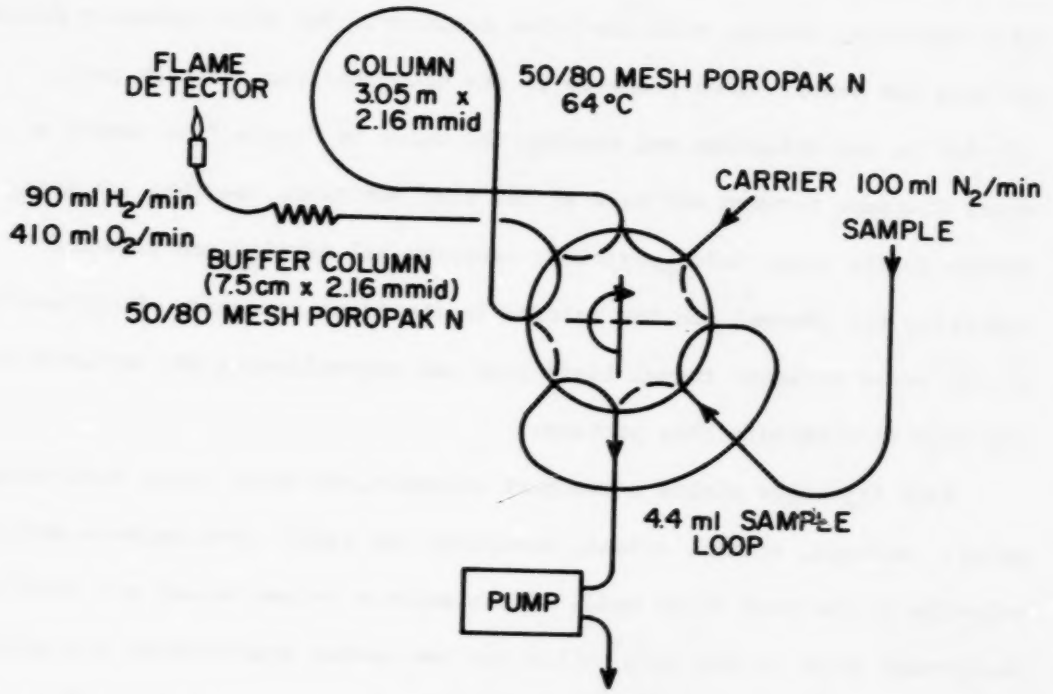
FLAME DETECTOR
COLUMN 3.05 m x 2.16 mmid
50/80 MESH POROPAK N 64 °C
CARRIER 100 ml N_2/min
SAMPLE
90 ml H_2/min
410 ml O_2/min
BUFFER COLUMN (7.5 cm x 2.16 mmid) 50/80 MESH POROPAK N
4.4 ml SAMPLE LOOP
PUMP

Figure 5. An eight-port, two-position automated sampling valve is at the heart of this hydrocarbon analysis chromatograph.

minimize line restrictions. To determine if the drift may have been caused by contamination the sample valve was moved 180° in relation to all plumbing connections. Neither the capillary nor Teflon bead buffer column

controlled the cyclic drift. As previously mentioned, only when the Poropak N column buffer was installed was the cyclic drift controlled.

Another problem affecting the instrument was thermal cycling caused by the room air conditioner. This problem was minimized when a small cardboard box was placed over the flame detector, a second cardboard box was placed over the whole instrument, and a deflector was attached to the room air conditioner to eliminate drafts around the chromatograph.

Baseline shifts, usually going completely off scale, were also caused by a recurring problem with the valve actuator. The valve actuator failed to turn the sample valve properly to its stop position, usually going too far in one direction and causing the valve to "cycle," or travel a short distance forward and back at one stop position, and then not going far enough at the other valve position, stopping all carrier gas flow and upsetting the thermal and ion balance in the flame detector. Modification of the valve actuator travel limit cams and repositioning the actuator were required to eliminate this problem.

Each injection yields a two part chromatogram which gives five measured peaks: methane, ethane, ethene, acetylene and higher hydrocarbons and other organics in the back flush mode. Since methane values exceed the world-wide background value of 890 ug/m^3 while the two carbon hydrocarbons are often less than 10 ug/m^3 it was necessary to record the signal at full (X1) and reduced (x20) sensitivity. A typical sequence is shown in Figure 6 for 15 July 1977. Only the methane is detectable on the lower trace; on this time scale the peak width is not discernable. The upper trace shows the two carbon hydrocarbons from the direct injection followed by the higher hydrocarbons backflushed through the detector after column reversal (labelled as

C_3^+ hydrocarbons). The peaks for all five components are of adequate size for measurement. Some characteristics of polluted air are evident in this tracing:

1) The ratio of the reactive hydrocarbon ethene to the unreactive hydrocarbon acetylene is appreciably lower in the midday reacted sample as compared to morning or evening sample.

2) The unreactive acetylene and ethane are larger in the morning

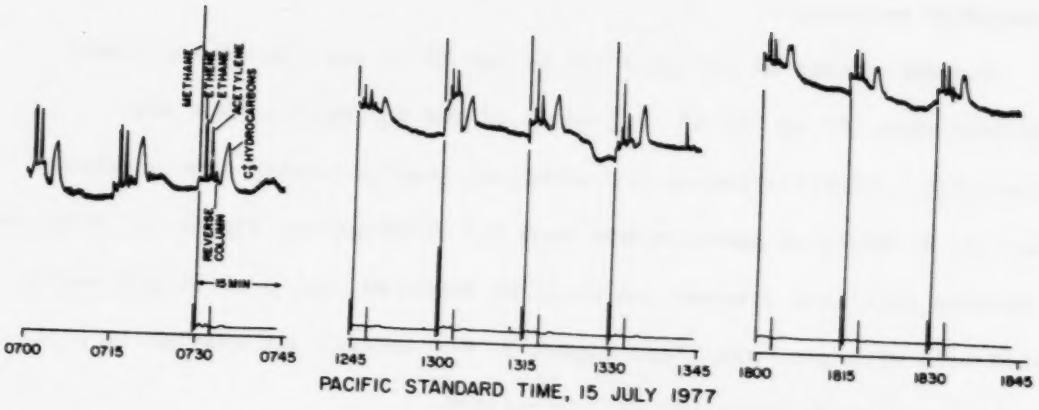

Figure 6. Representative hydrocarbon chromatograms showing morning, midday, and evening pollution.

than during the midday.

It does not clearly show on the sample chromatograms but the methane peak is preceded by another peak which seems to be related to the presence of carbon monoxide. At higher chart speeds the two peaks are seen to be nearly completely separated. This might prove useful but there is no apparent interference with the methane measurement.

Calibration

Both commercial calibration gas mixtures and special dilution mixes were used for calibration of the one and two carbon hydrocarbon peaks. The latter were prepared in low pressure oxygen tanks and were stable and suitable. Typical calibration results are shown in Table 3. The last column gives the concentration in (ug/M^3) which corresponsponds to one chart division of pen deflection. Thus it corresponds roughly to the minimum detectable quantity.

Concentrations as low as a few ug per M^3 of the C_2s (about 5 ppb) and less than 100 ug per M^3 (0.2 ppmC) of the C_3^+ hydrocarbon are detectable. Quantitation of the backflush peak presented some problems. Finally, a sample of gasoline was used for calibration, Figure 7. This gave a broader peak than propane, as would be expected, but peak height correlated well with peak area (see Figure 8) for ambient air samples so peak height was used to calculate concentrations.

The propane/methane gas mixture gave a backflush peak, due to propane, which was quite sharp whereas the ambient air peak was somewhat broader with some tailing. A mixture of C_8 hydrocarbons containing 0.10 ml 2,2,4-trimethyl-2-pentene, 0.35 ml xylene, and 0.55 ml 3-methyl heptane was

TABLE 3. CALIBRATION WITH LIGHT HYDROCARBONS.

Compound	Concentration ppb*	Concentration ug/m^3	Peak height scale divisions	Att. x	Response mv	K $mv/ug/m^3$	ug/m^3 division
Methane	1160	757	34	20	6.80	8.98×10^{-3}	1.11
Methane	58.8	38.3	35.7	1	0.357	9.32 " "	1.07
Ethane	49.8	60.9	25.5	1	0.255	4.19 " "	2.39
Ethene	51.0	58.3	32.2	1	0.322	5.53 " "	1.81
Acetylene	55.0	58.3	26.8	1	0.268	4.60 " "	2.17
Propane**	46.2	82.9	6.2	1	0.062	0.748" "	13.4
Propane**	607	1089	46	2	0.920	0.844" "	11.8

*ppb by moles ($298^{\circ}K$, 1 atm)

**backflush mode

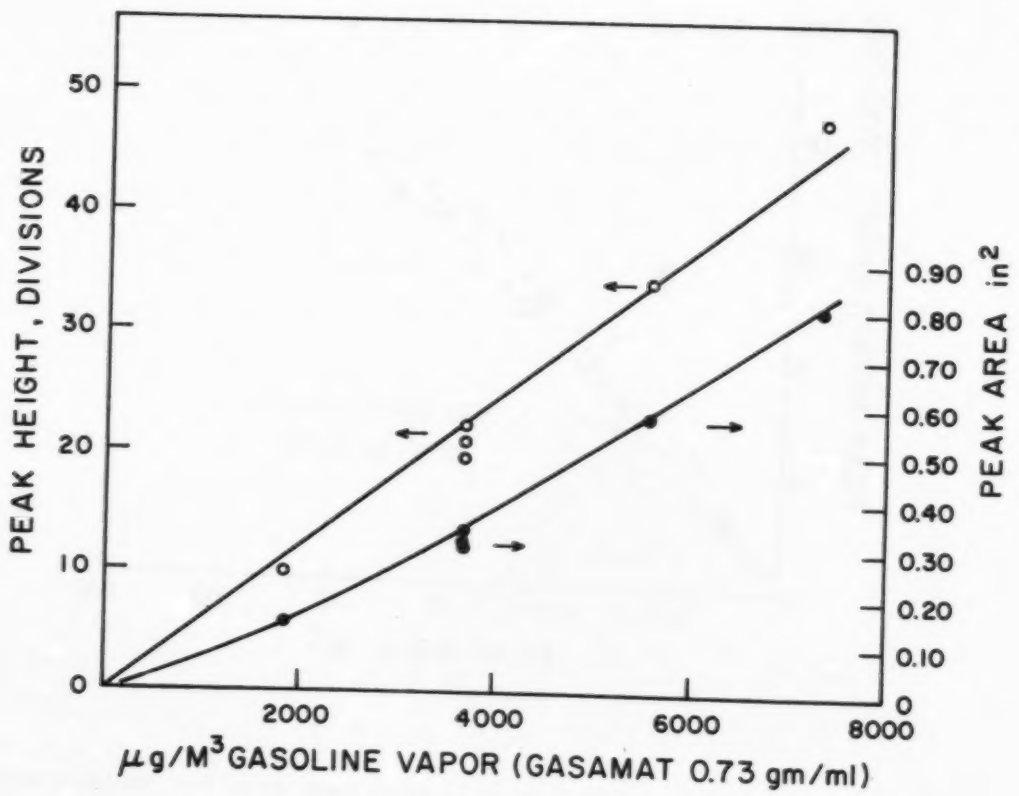

Figure 7. Peak height and peak area gave pair correlations with concentrations of a commercial gasoline.

prepared as a standard reference mixture to simulate gasoline vapor, but it was impossible to obtain repeatable results when sampling ppb concentration dilutions of this mixture. Similar problems were encountered when using xylene alone and n-heptane alone.

More repeatable data were obtained when small quantities of gasoline were vaporized in a 20 L bottle and dilutions of this mixture were sampled by the GC. Such data are shown in Table 4. Some differences in peak

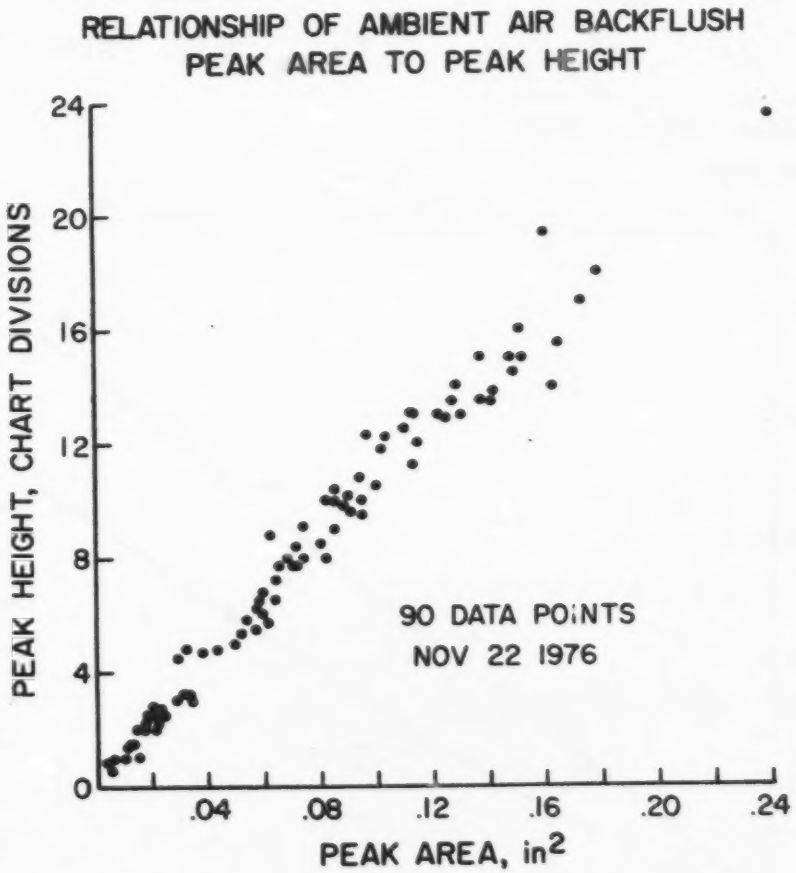

Figure 8. Peak heights correlated well with peak area for ambient air sample.

shape compared to ambient air are still observed, gasoline being somewhat broader at the base than the ambient air peak. These broader peaks resulted in a sensitivity about one order of magnitude lower for the gasoline.

TABLE 4. CALIBRATION WITH GASOLINE.

Concentration ug/m^3	Peak Height division	Peak Area in^2
1830	10.0	0.144
3660	19.6	0.315
3660	20.9	0.303
3660	22.3	0.338
5550	34.2	0.574
7322	47.8	0.851

Regular grade "Gasamat" brand gasoline
Specific gravity: 0.73 gm/ml

NITROGEN OXIDES

A chemiluminescence analyzer (TECO) was used to measure NO and total nitrogen oxides (by thermal conversion to NO). Typical records are shown in Figures 9, 10 and 11. For the 15 July 1977 record, the integrating bottle was in place and gave a much smoother record than the two earlier ones. Most users of these instruments wish to convert only NO_2 to NO so that the difference NO_x-NO can be equated to NO_2. Since PAN is a fragile molecule there is probably no way to prevent its conversion to NO so the NO_x-NO at least must be regarded as NO_2 + PAN. There is evidence also that nitrates and nitrites will also be reduced by NO by the catalyst. The NO_x records shown in the figures both indicate high NO_x levels in morning and evening with much smaller values in midday. The 17 December 1975 record shows a

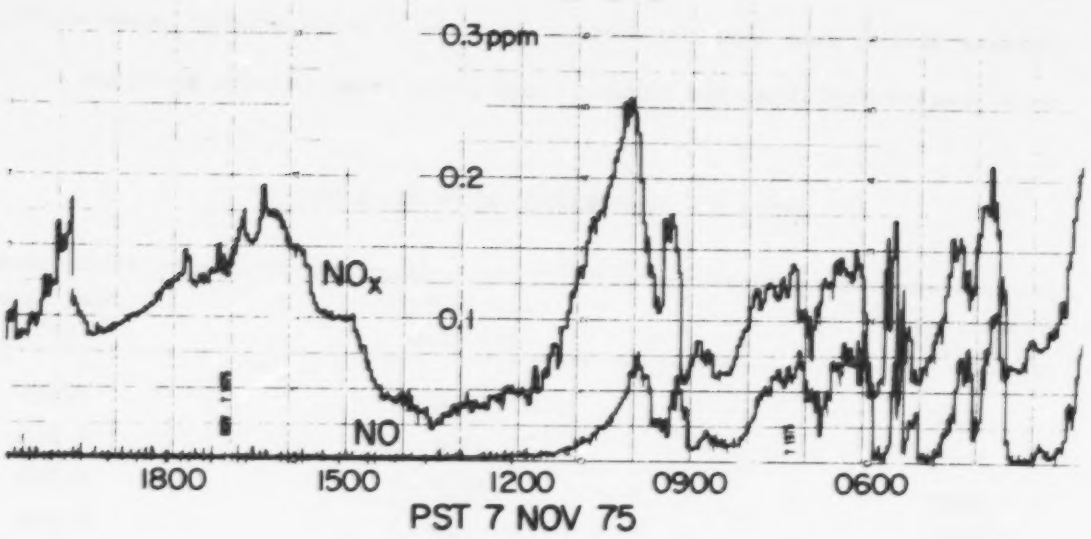

Figure 9. This fall day shows the high values of NO_x created by morning traffic which disappears in midday when the radiation inversion breaks.

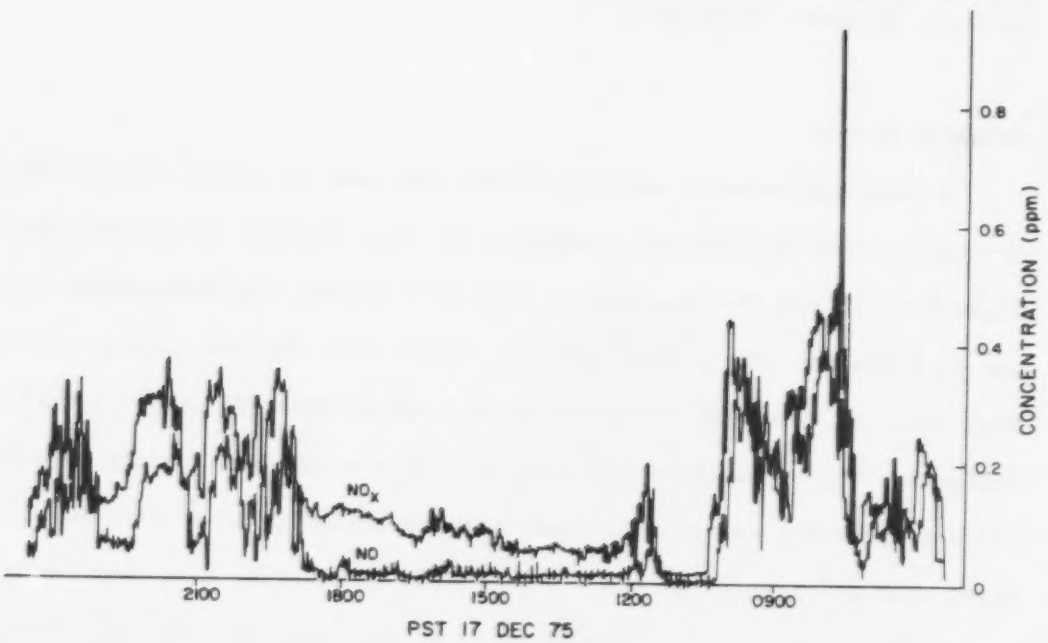

Figure 10. Very high NO_x/NO values on a December morning. Almost all the NO_x was NO. The spike at 0800, caused by a nearby tractor, led to an NO value which exceeded the NO_x.

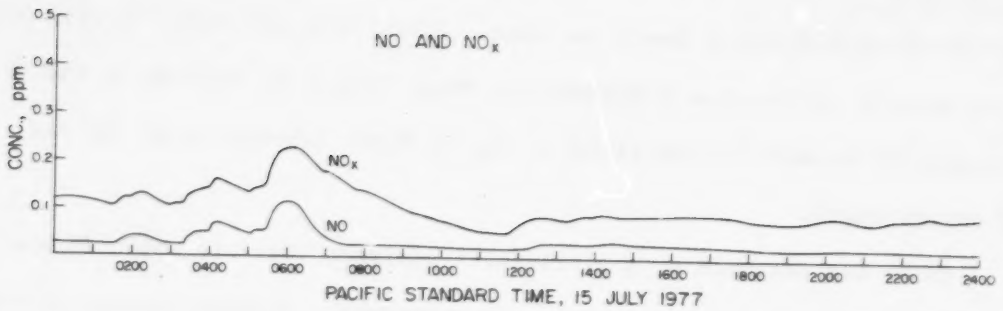

Figure 11. The NO_x/NO traces after installation of the integrating bottle. Both traces are much smoother than in Fig. 9 and 10. The persistent overnight NO_x must represent previous days pollution whereas the NO (note that it parallels the NO_x) represents new infusions of combustion gas.

spike of >0.9 ppm at 0745 which is attributed to a nearby farm tractor (the sampling site is in a "weather station" in the middle of an experimental agricultural field). The rarity of these events suggests that these local sources are not a serious interference with the experimental plan. The fact that this one NO reading exceeded the NO_x would lead to a negative NO_2 + PAN + NO - concentration. It points up the hazard involved in subtraction methods involving consecutive samples (such as the conventional THC - CH_4 = NMHC). The fraction of the NO_x which is NO gives an independent assessment of the degree of reaction.

OXIDANT AND OZONE

Two instruments are in operation for measurement of these two closely

related quantitites. Oxidant is measured by the potassium iodide procedure using a coulometric analyzer (Mast). This instrument has been in operation for many years. Formerly, the manual KI calibration procedure of the California Air Resource Board was used. Since this was found to give high readings the calibration procedure has been changed to conform to the UV photometric standard established at the El Monte laboratory of the Air Resources Board.

Ozone was measured by a ultraviolet analyzer (Dasibi) which is also coordinated with the photometric ozone standards. Typical records are shown in Figures 12 and 13. These records correspond to the NO_x traces of Figures 9 and 11. It appears now that the ultraviolet photometer can come close to qualifying as a primary standard (R. J. Paur, NYC ACS meeting, 1976) since the ultraviolet absorption spectrum is known with high accuracy and the other important variables are readily ascertainable (pressure, temperature, path-length).

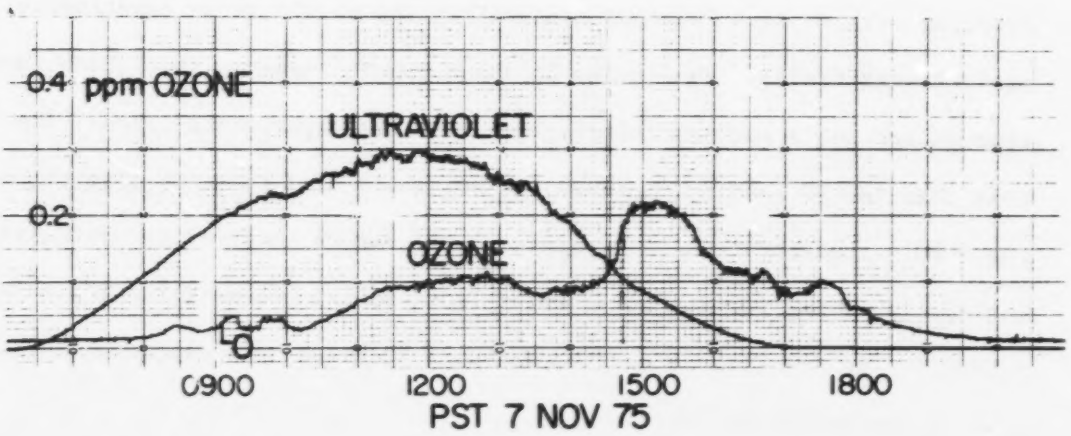

Figure 12. Typical ozone and ultraviolet radiation record early fall. Compare NO_x in Figure 9.

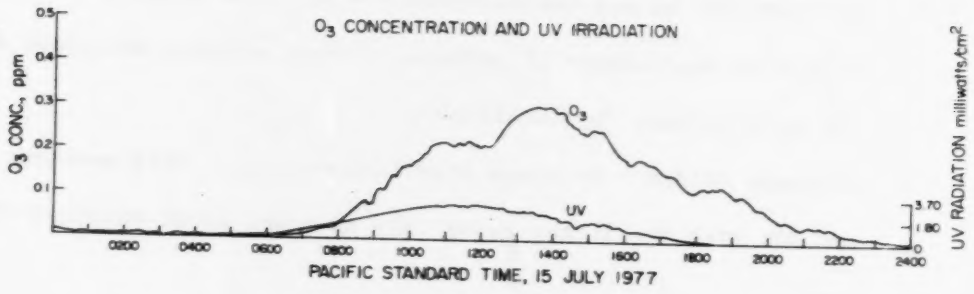

Figure 13. Summer record of ozone and ultraviolet.

PAN

An automatated PAN chromatograph (electron capture) operating on a 15-minute cycle has been in operation for many years. This was maintained in operation and calibration even though it did not play an important role in the present program.

LIGHT INTENSITY

An ultraviolet radiometer (Eppley Laboratories Model TUVR) was installed on the roof of the weather station to monitor total ultraviolet (295-385 nanometers, approximately). This instrument suffered a sudden unexplained loss of output signal twice during the program. Typical records are shown in Figures 12 and 13.

DATA REDUCTION

These five monitoring instruments were operated around the clock in the UCR weather station. To summarize the measurements which were made on a continuous or automatic basis:

1. Hydrocarbons by gas chromatography with flame ionization. Direct injection measurement of methane, ethane, ethene, acetylene and C3+ hydrocarbons (by backflush).
2. Nitrogen Oxides - By ozone chemiluminescence. This measures NO and NOx with the latter being take as equal total oxidized nitrogen.
3. Oxidant - By coulometric KI method.
4. Ozone - By UV absorption.
5. UV Intensity - By recording of UV meter.

The analytical data were recorded on strip charts since this was regarded as a pilot program automatic reduction of the chromatographic output would be difficult. Peak heights and deflections were read from the strip charts and entered into punch cards for machine handling. Sensitivity factors were also entered via punch cards. To make all data comparable with the 15 minute sampling interval of the chromatographs the other measurements were averaged over these same intervals. Five hydrocarbon measurements plus five other variables adds to 40 points per hour or 960 per day. Only machine handling makes this manageable. It facilitated grouping the data points according to ethene/acetylene ratio (indicative of degree of reaction) and other variables.

SECTION 5

RESULTS

Each instrument of course suffered its share of downtime so the major effort at data reduction was directed toward those days during which the most data, especially for hydrocarbon and nitrogen oxides, were available. Eventually the data for 61 days were reduced to machine readable form. If all instruments had produced full sets of data 61 x 960 = 58,560 concentrations would have been recorded. Even the incomplete set which was obtained represents a large manual effort. The strip chart values were read by hand first then into punch cards. This deck of cards constitutes the useful data output of the project. The contents of the cards were printed but it would clearly be hopeless to derive any useful conclusions by visual examination of data in this form.

The number of different manipulations possible for this data set is limited only by imagination. The major effort was directed toward tabulation of "conditional joint distributions." With ten variables (plus time) on the cards 45 different pairings are possible. Some of these would be meaningless so effort was concentrated on conditional distributions of the more interesting combinations. Photochemical smog conditions can be selected by the condition $O_3 > 60$ ug/m^3. The various conditional joint distributions are shown in Tables 5 to 15.

COMMENTS ON TABLES

As stated earlier ethene and acetylene were added to the C_3^+ (back-

flush peak) as a measure of the significant hydrocarbon. Methane was omitted for the traditional reasons: (1) it is present in amounts large enough to dominate the hydrocarbon, much of it (1.4 ppm = 887 ug/m^3) as worldwide background. (2) it is quite low in reactivity. Ethane was also omitted because it is attributed in large part to natural gas. It's inclusion might degrade any correlations dependent on auto emissions without making a large difference. It is also of low reactivity. Since the back flush peak also probably includes oxygenates a fitting heading might be nonmethane ethane organic (NMEO). The first six tables show joint distributions of these parameters with various others and with various conditions.

Table 5. This set (NMEO vs NO_x) should give a narrow band of entries sloping downward to the right if the emissions were always in the same ratio and if atmospheric reaction affected them equally. Part a which includes data from all 61 days shows a broader spread than anticipated. Some of this spread might arise from failure to measure NMEO and NO_x on the same air sample. Failure to coordinate the time scales precisely would cause this if the concentrations are fluctuating rapidly. This was the reason for inserting the integrator bottle into the sampling line on April 19, 1977. The distribution after that date (Table Ib) was somewhat narrower but still fairly broad. Tables Ic and Id compare these same joint distributions for reacted and unreacted samples. The ratio of NMHC to NO_x is larger in the reacted samples as though more NO_x than hydrocarbon were lost by reaction. Tables Ie and If show this same distribution for morning hours and evening hours. These show similar patterns but the evening hours appear to have more high values.

Table 6. This shows the NMEO in joint distribution with NO. As expected this shows many NO values below the minimum of 50 ug/m^3 corresponding to reacted samples.

Table 7. This joint distribution of NMEO with ozone shows an interesting bimodal plot. The low O_3 values correspond to unreacted mixtures whereas the low hydrocarbon values represent photochemical smog. Some high ozone values (>400 ug/m^3; 0.21 ppm) were recorded for hydrocarbon values under 500 ug/m^3 ($\simeq$0.78 ppm).

Table 8. The joint distribution of non-methane-ethane-organic with acetylene. This interesting set of tables makes use of the relative inertness of acetylene and its unique association with auto exhaust. All three of these distributions show a relatively narrow spread. This clearly illustrates the strong dependence of NMEO on engine exhaust. The few outliers with high NMEO at low acetylene (<10 ug/m^3) may be due to unusual discharges from other sources (i.e., pesticide application on the surrounding agricultural fields). The effect of photochemical reaction can be seen by comparing 8b (smog, O_3 > 160 ug/m^3) with 8c (unreacted emissions, NO > 60 ug/m^3). Loss of NMEO relative to acetylene is not discernable in these data. Since acetylene is of low reactivity the average NMEO must produce other organics with little loss of effect on the flame ionization detector. Based on these three tables it would be hard to justify any "back extrapolation" to a higher hydrocarbon value in the unreacted state.

Table 9. The joint distribution of NMEO with ethane shows a fair correlation even though the former is derived from auto exhaust and the latter from natural gas. There is no definite bias for either morning

or evening.

Table 10. These joint distributions with methane show larger spreads because of the background methane concentrations.

Table 11. These joint distributions of acetylene with ethene reveal the higher reactivity of the former. 11d shows the good correlation in the unreacted samples (NO > 60 ug/m^3) with the weights of the two hydrocarbons being about equal (prior work indicated a weight ratio of 0.9). Table 11c shows the reacted (ozone > 160 ug/m^3) samples; the lowered relative amount of ethene caused by reaction (e.g. in the unreacted samples the maximum frequency (62) occurs in the 30-40 by 30-40 bracket (Table 11d) but the maximum frequency (21) for this acetylene level occurs in the 20-30 ug/m^3 ethene bracket for reacted samples.) If only higher ozone levels were considered, e.g., >300 ug/m^3, there would be fewer data but a larger depletion of ethene with respect to acetylene would be seen.

Table 12. These joint distributions of acetylene and methane again show how a degree of correlation is produced by common trapping of hydrocarbons from different sources. The spreads are so broad that no trends are evident.

Table 13. The joint distribution of ethane and methane do not show as narrow a spread as expected for hydrocarbons with a common origin. Perhaps there is variability with time in the ethane content of natural gas.

Table 14. This joint distribution of ozone and oxidant shows the expected good correlation. Oxidant values seem to be systematically low; they were corrected for neither positive (NO_2, PAN) nor negative (SO_2) interferences.

Table 15. This joint distribution of ozone with NO_x at NMEO above 160 ug/m^3 shows a bimodal distribution between the two variables. This reflects the contrast between reacted and unreacted samples. It may be noted that 3469 out of 5092 recorded values were above 160 ug $NMEO/m^3$.

Preparation of this type of data analysis inevitably invites consideration of alternative modes of analysis which could be done and which might be revealing. Conditional linear regressions would be one tempting procedure. For example, ethene regressed with acetylene at various oxidant levels and for high values of NO/NO_x would reveal the selective loss of the more reactive hydrocarbon. Regression of NMEO with acetylene with the same conditions would explore the extent to which this is a "net" loss of higher molecular weight organic due to reaction.

5a. JOINT DISTRIBUTION OF NON METHANE/ETHANE ORGANICS (ETHENE PLUS ACETYLENE PLUS BACK FLUSH PEAK) AND NO_x [NO + NO_x + PAN + NITRATES (?)] WEIGHT AS NO_2.

a. ALL REDUCED DATA

NUX UG/M3	(C2H4, C2H2, C3+) UG/M3 **** 0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
0- < 50	413	0	0	0	0	0	0	0	0	0	0	413
50- < 100	1114	60	4	0	0	0	0	0	0	0	0	1178
100- < 150	672	229	26	3	0	0	0	0	0	0	0	930
150- < 200	288	268	38	23	10	1	2	0	0	0	0	630
200- < 250	154	194	36	29	16	1	0	0	0	0	0	430
250- < 300	68	116	40	34	17	2	0	0	0	0	0	277
300- < 350	23	81	32	20	22	1	1	0	0	0	0	180
350- < 400	16	35	19	11	11	4	0	0	0	0	0	96
400- < 450	4	31	23	6	12	4	0	0	0	0	0	80
450- < 500	1	14	15	8	2	4	1	0	0	0	0	45
500- < 550	0	11	23	3	4	2	0	0	0	0	0	43
550- < 600	0	4	11	3	3	4	1	1	0	0	0	27
600- < 650	1	3	1	1	2	3	0	0	0	0	0	12
650- < 700	0	2	1	2	1	2	0	0	0	0	0	8
700- < 750	0	0	4	3	1	1	2	0	0	0	0	11
750- < 800	0	1	1	0	0	0	0	0	0	0	0	2
800- < 850	0	0	0	1	1	0	0	0	1	0	0	3
850- < 900	0	0	0	0	0	2	0	0	0	0	0	2
900- < 950	0	0	0	0	0	3	0	0	0	0	0	3
950- < 1000	0	0	0	0	0	0	0	0	0	0	0	0
TOTAL	2754	1049	275	147	102	34	7	1	1	0		4370

5b. JOINT DISTRIBUTION OF NON METHANE/ETHANE ORGANICS (ETHENE PLUS ACETYLENE PLUS BACK FLUSH PEAK) AND NO_x [NO + NO_x + PAN + NITRATES (?)] WEIGHT AS NO_2.

b. AFTER INSTALLATION OF INTEGRATOR BOTTLE

(C2H4, C2H2, C3+) UG/M3 **** AFTER 4/19/77

NOX UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
0- < 50	72	0	0	0	0	0	0	0	0	0	0	72
50- < 100	346	5	0	0	0	0	0	0	0	0	0	351
100- < 150	150	108	0	0	0	0	0	0	0	0	0	258
150- < 200	34	99	0	0	0	0	0	0	0	0	0	133
200- < 250	16	54	0	0	0	0	0	0	0	0	0	70
250- < 300	13	33	1	0	0	0	0	0	0	0	0	47
300- < 350	2	14	4	0	0	0	0	0	0	0	0	20
350- < 400	0	2	0	0	0	0	0	0	0	0	0	2
400- < 450	0	5	0	0	0	0	0	0	0	0	0	5
450- < 500	0	0	1	0	0	0	0	0	0	0	0	1
500- < 550	0	0	0	0	0	0	0	0	0	0	0	0
550- < 600	0	0	0	0	0	0	0	0	0	0	0	0
600- < 650	0	0	0	0	0	0	0	0	0	0	0	0
650- < 700	0	0	0	0	0	0	0	0	0	0	0	0
700- < 750	0	0	0	0	0	0	0	0	0	0	0	0
750- < 800	0	0	0	0	0	0	0	0	0	0	0	0
800- < 850	0	0	0	0	0	0	0	0	0	0	0	0
850- < 900	0	0	0	0	0	0	0	0	0	0	0	0
900- < 950	0	0	0	0	0	0	0	0	0	0	0	0
950- < 1000	0	0	0	0	0	0	0	0	0	0	0	0
TOTAL	633	320	6	0	0	0	0	0	0	0	0	959

5c. JOINT DISTRIBUTION OF NON METHANE/ETHANE ORGANICS (ETHENE PLUS ACETYLENE PLUS BACK FLUSH PEAK) AND NO_x [NO + NO_x + PAN + NITRATES (?)] WEIGHT AS NO_2.

c. FOR OZONE EXCEEDING THE STANDARD

(C2H4, C2H2, C3+) UG/M3 **** O3 >= 160 UG/M3

NOX UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
0- < 50	49	0	0	0	0	0	0	0	0	0	0	49
50- < 100	239	22	0	0	0	0	0	0	0	0	0	261
100- < 150	62	54	3	2	0	0	0	0	0	0	0	121
150- < 200	8	23	7	8	7	0	0	0	0	0	0	53
200- < 250	1	4	1	3	6	0	0	0	0	0	0	15
250- < 300	0	0	0	0	2	0	0	0	0	0	0	2
300- < 350	0	0	0	2	2	0	0	0	0	0	0	4
350- < 400	0	0	0	0	0	0	0	0	0	0	0	0
400- < 450	0	0	0	0	1	0	0	0	0	0	0	1
450- < 500	0	0	0	0	0	0	0	0	0	0	0	0
500- < 550	0	0	0	0	0	0	0	0	0	0	0	0
550- < 600	0	0	0	0	0	0	0	0	0	0	0	0
600- < 650	0	0	0	0	0	0	0	0	0	0	0	0
650- < 700	0	0	0	0	0	0	0	0	0	0	0	0
700- < 750	0	0	0	0	0	0	0	0	0	0	0	0
750- < 800	0	0	0	0	0	0	0	0	0	0	0	0
800- < 850	0	0	0	0	0	0	0	0	0	0	0	0
850- < 900	0	0	0	0	0	0	0	0	0	0	0	0
900- < 950	0	0	0	0	0	0	0	0	0	0	0	0
950- < 1000	0	0	0	0	0	0	0	0	0	0	0	0
TOTAL	359	103	11	15	18	0	0	0	0	0	0	506

5d. JOINT DISTRIBUTION OF NON METHANE/ETHANE ORGANICS (ETHENE PLUS ACETYLENE PLUS BACK FLUSH PEAK) AND NO_x [NO + NO_x + PAN + NITRATES (?)] WEIGHT AS NO_2.

d. FOR UNREACTED AIR (HIGH NITRIC OXIDE)

(C2H4, C2H2, C3+) UG/M3 **** NO >= 60 UG/M3

NOX UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
0- < 50	0	0	0	0	0	0	0	0	0	0	0	0
50- < 100	1	0	0	0	0	0	0	0	0	0	0	1
100- < 150	14	6	0	0	0	0	0	0	0	0	0	20
150- < 200	92	33	2	0	0	0	1	0	0	0	0	148
200- < 250	125	97	9	0	1	1	0	0	0	0	0	253
250- < 300	63	90	21	17	6	2	0	0	0	0	0	199
300- < 350	22	76	23	9	5	0	1	0	0	0	0	136
350- < 400	15	34	19	11	7	0	0	0	0	0	0	86
400- < 450	4	31	23	6	4	3	0	0	0	0	0	71
450- < 500	1	14	14	8	1	4	1	0	0	0	0	43
500- < 550	0	11	23	3	4	2	0	0	0	0	0	43
550- < 600	0	4	11	3	3	4	1	1	0	0	0	27
600- < 650	1	3	2	1	2	3	0	0	0	0	0	12
650- < 700	0	2	1	2	1	2	0	0	0	0	0	8
700- < 750	0	0	4	3	1	1	2	0	0	0	0	11
750- < 800	0	1	1	0	0	0	0	0	0	0	0	2
800- < 850	0	0	0	1	1	0	0	0	1	0	0	3
850- < 900	0	0	0	0	0	2	0	0	0	0	0	2
900- < 950	0	0	0	0	0	3	0	0	0	0	0	3
950- < 1000	0	0	0	0	0	0	0	0	0	0	0	0
TOTAL	338	402	153	64	36	27	6	1	1	0		1028

5e. JOINT DISTRIBUTION OF NON METHANE/ETHANE ORGANICS (ETHENE PLUS ACETYLENE PLUS BACK FLUSH PEAK) AND NO_x [NO + NO_x + PAN + NITRATES (?)] WEIGHT AS NO_2.

e. FOR MORNING HOURS

(C2H4, C2H2, C3+) UG/M3 **** 0600 - 0900 PST

NOX UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
0- < 50	16	0	0	0	0	0	0	0	0	0		16
50- < 100	76	1	0	0	0	0	0	0	0	0		77
100- < 150	78	13	6	0	0	0	0	0	0	0		97
150- < 200	50	39	5	1	0	0	0	0	0	0		95
200- < 250	42	23	3	0	0	1	0	0	0	0		69
250- < 300	23	17	2	1	0	1	0	0	0	0		44
300- < 350	8	17	5	4	2	0	0	0	0	0		36
350- < 400	6	9	1	0	0	0	0	0	0	0		16
400- < 450	1	7	4	0	1	0	0	0	0	0		13
450- < 500	1	4	2	0	0	0	0	0	0	0		7
500- < 550	0	0	3	0	0	0	0	0	0	0		3
550- < 600	0	1	3	0	0	0	0	1	0	0		5
600- < 650	1	1	0	0	0	0	0	0	0	0		2
650- < 700	0	1	1	0	0	0	0	0	0	0		2
700- < 750	0	0	2	0	0	0	0	0	0	0		2
750- < 800	0	0	0	0	0	0	0	0	0	0		0
800- < 850	0	0	0	0	0	0	0	0	0	0		0
850- < 900	0	0	0	0	0	0	0	0	0	0		0
900- < 950	0	0	0	0	0	0	0	0	0	0		0
950- < 1000	0	0	0	0	0	0	0	0	0	0		0
TOTAL	302	133	37	6	3	2	0	1	0	0		484

5f. JOINT DISTRIBUTION OF NON METHANE/ETHANE ORGANICS (ETHENE PLUS ACETYLENE PLUS BACK FLUSH PEAK) AND NO_x [NO + NO_x + PAN + NITRATES (?)] WEIGHT AS NO_2.

f. FOR EVENING HOURS

(C2H4, C2H2, C3+) UG/M3 **** 2000 - 2400 PST

NOX UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
0- < 50	35	0	0	0	0	0	0	0	0	0		35
50- < 100	127	4	1	0	0	0	0	0	0	0		132
100- < 150	131	46	2	0	0	0	0	0	0	0		179
150- < 200	70	61	8	6	6	1	0	0	0	0		152
200- < 250	32	27	6	20	8	0	0	0	0	0		93
250- < 300	17	17	4	8	8	0	0	0	0	0		54
300- < 350	10	20	6	7	8	0	1	0	0	0		52
350- < 400	6	9	7	2	3	2	0	0	0	0		29
400- < 450	0	11	4	5	6	1	0	0	0	0		27
450- < 500	0	5	7	3	1	3	0	0	0	0		19
500- < 550	0	3	8	2	2	2	0	0	0	0		17
550- < 600	0	2	3	3	2	3	1	0	0	0		14
600- < 650	0	1	2	1	1	3	0	0	0	0		8
650- < 700	0	1	0	1	1	2	0	0	0	0		5
700- < 750	0	0	2	2	1	1	2	0	0	0		8
750- < 800	0	1	1	0	0	0	0	0	0	0		2
800- < 850	0	0	0	0	1	0	0	0	1	0		2
850- < 900	0	0	0	0	0	2	0	0	0	0		2
900- < 950	0	0	0	0	0	2	0	0	0	0		2
950- < 1000	0	0	0	0	0	0	0	0	0	0		0
TOTAL	428	208	61	60	48	22	4	0	1	0		832

TABLE 6. JOINT DISTRIBUTION OF NON METHANE/ETHANE ORGANICS (ETHENE PLUS ACETYLENE PLUS BACK FLUSH PEAK) AND NO (WEIGHT AS NO).

	(C2H4, C2H2, C3+) UG/M3 ****										
NO UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
0- < 50	2340	576	112	77	62	5	1	0	0	0		3173
50- < 100	279	236	42	23	17	6	1	0	0	0		604
100- < 150	91	129	38	19	7	8	1	0	0	0		293
150- < 200	25	56	29	8	5	5	2	0	0	0		130
200- < 250	7	28	29	7	4	1	0	0	0	0		76
250- < 300	2	20	13	9	3	4	2	1	0	0		54
300- < 350	0	7	7	4	2	3	0	0	0	0		23
350- < 400	0	2	4	0	0	0	0	0	1	0		7
400- < 450	0	0	2	0	0	3	0	0	0	0		5
450- < 500	0	0	0	0	2	0	0	0	0	0		2
500- < 550	0	0	0	0	0	0	0	0	0	0		0
550- < 600	0	0	0	0	0	0	0	1	0	0		1
600- < 650	0	0	0	0	0	0	0	0	0	0		0
650- < 700	0	0	0	0	1	0	0	0	0	0		1
700- < 750	0	0	0	0	0	0	0	0	0	0		0
750- < 800	0	0	0	0	0	0	0	0	0	0		0
800- < 850	0	0	0	0	0	0	0	0	0	0		0
850- < 900	0	0	0	0	0	0	0	0	0	0		0
900- < 950	0	0	0	0	0	0	0	0	0	0		0
950- < 1000	0	0	0	0	0	0	0	0	0	0		0
TOTAL	2744	1054	276	147	103	35	7	2	1	0		4369

TABLE 7. JOINT DISTRIBUTION OF NON METHANE/ETHANE ORGANICS WITH OZONE.

	(C2H4, C2H2, C3+) UG/M3 ****										
O3 UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
0- < 50	1658	821	210	98	48	24	6	2	1	0		2868
50- < 100	440	82	40	27	28	11	1	0	0	0		629
100- < 150	269	34	14	7	7	0	0	0	0	0		331
150- < 200	121	31	4	3	5	0	0	0	0	0		164
200- < 250	116	29	1	4	8	0	0	0	0	0		158
250- < 300	77	19	3	3	3	0	0	0	0	0		105
300- < 350	30	13	0	2	0	0	0	0	0	0		45
350- < 400	25	10	0	2	1	0	0	0	0	0		38
400- < 450	11	4	3	0	1	0	0	0	0	0		19
450- < 500	0	1	0	0	0	0	0	0	0	0		1
TOTAL	2747	1044	275	146	101	35	7	2	1	0		4358

TABLE 8a. JOINT DISTRIBUTION OF NON METHANE/ETHANE ORGANICS WITH ACETYLENE
a. ALL REDUCED DATA

	(C2H4, C2H2, C3+) UG/M3 ****										
C2H2 UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
0- < 10	2611	178	1	0	1	0	2	0	0	0		2793
10- < 20	148	804	50	2	0	2	0	0	0	0		1006
20- < 30	0	72	193	44	2	1	1	0	0	0		313
30- < 40	0	1	30	93	72	11	1	0	0	0		208
40- < 50	0	0	3	8	21	15	0	1	0	0		48
50- < 60	0	0	0	0	6	5	1	0	1	0		13
60- < 70	0	1	0	0	0	1	2	0	0	0		4
70- < 80	0	0	0	0	1	0	0	1	0	0		2
80- < 90	0	0	0	0	0	0	0	0	0	0		0
90- < 100	0	0	0	0	0	0	0	0	0	0		0
TOTAL	2759	1056	277	147	103	35	7	2	1	0		4387

TABLE 8b. JOINT DISTRIBUTION OF NON METHANE/ETHANE ORGANICS WITH ACETYLENE
b. OZONE ABOVE STANDARD

	(C2H4, C2H2, C3+) UG/M3 **** O3 >= 160 UG/M3										
C2H2 UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
0- < 10	341	32	0	0	0	0	0	0	0	0		373
10- < 20	18	66	2	0	0	0	0	0	0	0		86
20- < 30	0	5	8	6	0	0	0	0	0	0		19
30- < 40	0	0	1	7	18	0	0	0	0	0		26
40- < 50	0	0	0	2	0	0	0	0	0	0		2
50- < 60	0	0	0	0	0	0	0	0	0	0		0
60- < 70	0	0	0	0	0	0	0	0	0	0		0
70- < 80	0	0	0	0	0	0	0	0	0	0		0
80- < 90	0	0	0	0	0	0	0	0	0	0		0
90- < 100	0	0	0	0	0	0	0	0	0	0		0
TOTAL	359	103	11	15	18	0	0	0	0	0		506

TABLE 8c. JOINT DISTRIBUTION OF NON METHANE/ETHANE ORGANICS WITH ACETYLENE
c. UNREACTED AIR, NO ABOVE 60 ug/m3 (0.05 ppm).

	(C2H4, C2H2, C3+) UG/M3 **** NO > 60 UG/M3										
C2H2 UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
0- < 10	279	33	0	0	1	0	1	0	0	0		314
10- < 20	62	324	15	0	0	2	0	0	0	0		403
20- < 30	0	48	112	15	1	1	1	0	0	0		178
30- < 40	0	1	24	45	20	7	1	0	0	0		98
40- < 50	0	0	3	4	13	13	0	1	0	0		34
50- < 60	0	0	0	0	1	4	1	0	1	0		7
60- < 70	0	1	0	0	0	1	2	0	0	0		4
70- < 80	0	0	0	0	1	0	0	1	0	0		2
80- < 90	0	0	0	0	0	0	0	0	0	0		0
90- < 100	0	0	0	0	0	0	0	0	0	0		0
TOTAL	341	407	154	64	37	28	6	2	1	0		1040

TABLE 9abc. JOINT DISTRIBUTION OF NON METHANE/ETHANE ORGANICS WITH ETHANE
a. ALL REDUCED DATA, b. MORNING, c. EVENTING.

(C2H4, C2H2, C3+) UG/M3 ****

C2H6 UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
0- < 10	2151	52	0	0	0	0	0	0	0	0		2203
10- < 20	600	727	49	2	1	1	2	0	0	0		1382
20- < 30	5	254	98	15	4	1	0	1	0	0		378
30- < 40	0	19	112	28	4	0	1	0	0	0		164
40- < 50	0	1	17	63	19	4	0	0	0	0		104
50- < 60	0	1	1	36	39	6	1	1	0	0		85
60- < 70	0	0	0	2	34	22	3	0	1	0		62
70- < 80	0	0	0	0	2	0	0	0	0	0		2
80- < 90	0	0	0	1	0	1	0	0	0	0		2
90- < 100	0	0	0	0	0	0	0	0	0	0		0
TOTAL	2756	1054	277	147	103	35	7	2	1	0		4382

(C2H4, C2H2, C3+) UG/M3 **** 0600 - 0900 PST

C2H6 UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
0- < 10	219	10	0	0	0	0	0	0	0	0		229
10- < 20	81	78	12	0	0	0	0	0	0	0		171
20- < 30	2	46	11	0	1	1	0	0	0	0		61
30- < 40	0	2	14	1	0	0	0	0	0	0		17
40- < 50	0	0	1	5	3	1	0	0	0	0		10
50- < 60	0	0	0	0	0	0	0	1	0	0		1
60- < 70	0	0	0	0	0	0	0	0	0	0		0
70- < 80	0	0	0	0	0	0	0	0	0	0		0
80- < 90	0	0	0	0	0	0	0	0	0	0		0
90- < 100	0	0	0	0	0	0	0	0	0	0		0
TOTAL	302	136	38	6	4	2	0	1	0	0		489

(C2H4, C2H2, C3+) UG/M3 **** 2000 - 2400 PST

C2H6 UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
0- < 10	354	11	0	0	0	0	0	0	0	0		365
10- < 20	73	164	8	1	0	0	0	0	0	0		246
20- < 30	1	29	32	8	2	0	0	0	0	0		72
30- < 40	0	4	18	4	2	0	1	0	0	0		29
40- < 50	0	0	3	29	8	2	0	0	0	0		42
50- < 60	0	0	0	16	19	4	1	0	0	0		40
60- < 70	0	0	0	1	16	17	2	0	1	0		37
70- < 80	0	0	0	0	1	0	0	0	0	0		1
80- < 90	0	0	0	1	0	0	0	0	0	0		1
90- < 100	0	0	0	0	0	0	0	0	0	0		0
TOTAL	428	208	61	60	48	23	4	0	1	0		633

TABLE 10ab. JOINT DISTRIBUTION OF NON METHANE/ETHANE ORGANICS WITH METHANE
a. ALL REDUCED DATA, b. MORNING.

(C2H4, C2H2, C3+) UG/M3 ****

CH4 UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
700- < 800	224	0	0	0	0	0	0	0	0	0		224
800- < 900	539	2	0	0	0	0	0	0	0	0		541
900- < 1000	480	83	0	0	0	0	0	0	0	0		563
1000- < 1100	254	208	3	0	1	0	1	0	0	0		467
1100- < 1200	632	145	5	0	0	0	0	0	0	0		782
1200- < 1300	216	176	19	0	0	0	1	0	0	0		412
1300- < 1400	56	144	56	3	2	1	0	0	0	0		262
1400- < 1500	17	65	52	20	5	0	0	0	0	0		159
1500- < 1600	10	30	34	23	16	1	1	0	0	0		115
1600- < 1700	2	8	27	26	10	10	1	0	0	0		84
1700- < 1800	4	1	8	10	6	1	0	0	0	0		30
1800- < 1900	1	2	2	8	11	3	2	0	0	0		29
1900- < 2000	1	3	3	4	4	5	0	0	1	0		21
TOTAL	2436	867	209	94	55	21	6	0	1	0		3689

(C2H4, C2H2, C3+) UG/M3 **** 0600 - 0900 PST

CH4 UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
700- < 800	15	0	0	0	0	0	0	0	0	0		15
800- < 900	49	0	0	0	0	0	0	0	0	0		49
900- < 1000	67	6	0	0	0	0	0	0	0	0		73
1000- < 1100	20	15	2	0	0	0	0	0	0	0		37
1100- < 1200	70	25	1	0	0	0	0	0	0	0		96
1200- < 1300	45	30	3	0	0	0	0	0	0	0		78
1300- < 1400	7	14	6	0	1	0	0	0	0	0		28
1400- < 1500	2	8	2	0	0	0	0	0	0	0		12
1500- < 1600	1	6	3	0	0	0	0	0	0	0		10
1600- < 1700	1	1	9	0	0	0	0	0	0	0		11
1700- < 1800	0	0	1	0	0	0	0	0	0	0		1
1800- < 1900	0	0	0	4	2	1	0	0	0	0		7
1900- < 2000	0	0	0	1	1	0	0	0	0	0		2
TOTAL	277	105	27	5	4	1	0	0	0	0		419

TABLE 10cd. JOINT DISTRIBUTION OF NON METHANE/ETHANE ORGANICS WITH METHANE
c. EVENINGS, d. OZONE ABOVE STANDARD.

(C2H4, C2H2, C3+) UG/M3 **** 2000 - 2400 PST

CH4 UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
700- < 800	21	0	0	0	0	0	0	0	0	0		21
800- < 900	75	2	0	0	0	0	0	0	0	0		77
900- < 1000	88	30	0	0	0	0	0	0	0	0		118
1000- < 1100	50	61	1	0	0	0	0	0	0	0		112
1100- < 1200	106	25	1	0	0	0	0	0	0	0		132
1200- < 1300	21	29	1	0	0	0	0	0	0	0		51
1300- < 1400	1	31	19	1	0	0	0	0	0	0		52
1400- < 1500	0	6	13	15	3	0	0	0	0	0		37
1500- < 1600	0	1	8	8	8	0	1	0	0	0		26
1600- < 1700	0	0	4	9	5	8	1	0	0	0		27
1700- < 1800	1	0	1	6	3	1	0	0	0	0		12
1800- < 1900	0	0	1	0	4	2	2	0	0	0		9
1900- < 2000	0	0	0	2	0	3	0	0	1	0		6
TOTAL	363	185	49	41	23	14	4	0	1	0		680

(C2H4, C2H2, C3+) UG/M3 **** O3 >= 160 UG/M3

CH4 UG/M3	0 -	500 -	1000 -	1500 -	2000 -	2500 -	3000 -	3500 -	4000 -	4500 -	5000	TOTAL
700- < 800	52	0	0	0	0	0	0	0	0	0		52
800- < 900	127	0	0	0	0	0	0	0	0	0		127
900- < 1000	104	13	0	0	0	0	0	0	0	0		117
1000- < 1100	37	27	0	0	0	0	0	0	0	0		64
1100- < 1200	6	5	0	0	0	0	0	0	0	0		11
1200- < 1300	5	8	0	0	0	0	0	0	0	0		13
1300- < 1400	3	2	0	0	0	0	0	0	0	0		5
1400- < 1500	6	6	1	3	0	0	0	0	0	0		16
1500- < 1600	2	8	2	2	3	0	0	0	0	0		17
1600- < 1700	1	2	1	0	4	0	0	0	0	0		8
1700- < 1800	0	0	0	0	0	0	0	0	0	0		0
1800- < 1900	0	0	0	0	0	0	0	0	0	0		0
1900- < 2000	0	0	0	0	0	0	0	0	0	0		0
TOTAL	343	71	4	5	7	0	0	0	0	0		430

TABLE 11ab. JOINT DISTRIBUTION OF ACETYLENE AND ETHENE
a. ALL REDUCED DATA, b. DATA WITH INTEGRATOR BOTTLE.

C2H2 UG/M3 **

C2H4 UG/M3	0 -	10 -	20 -	30 -	40 -	50 -	60 -	70 -	80 -	90 -	100	TOTAL
0- < 10	2871	141	1	0	0	0	0	0	0	0		3013
10- < 20	126	830	74	2	1	0	0	0	0	0		1033
20- < 30	0	46	205	88	1	0	0	0	0	0		340
30- < 40	0	0	35	97	18	1	0	0	0	0		151
40- < 50	0	0	0	21	18	5	0	0	0	0		44
50- < 60	0	0	0	0	11	6	0	0	0	0		17
60- < 70	0	0	0	0	0	2	2	1	0	0		5
70- < 80	0	0	0	0	0	0	2	1	0	0		3
80- < 90	0	0	0	0	0	0	0	0	0	0		0
90- < 100	0	0	0	0	0	0	0	0	0	0		0
TOTAL	2997	1017	315	208	49	14	4	2	0	0		4606

C2H2 UG/M3 ** AFTER 4/19/77

C2H4 UG/M3	0 -	10 -	20 -	30 -	40 -	50 -	60 -	70 -	80 -	90 -	100	TOTAL
0- < 10	727	40	0	0	0	0	0	0	0	0		767
10- < 20	21	205	3	0	0	0	0	0	0	0		229
20- < 30	0	0	0	0	0	0	0	0	0	0		0
30- < 40	0	0	0	0	0	0	0	0	0	0		0
40- < 50	0	0	0	0	0	0	0	0	0	0		0
50- < 60	0	0	0	0	0	0	0	0	0	0		0
60- < 70	0	0	0	0	0	0	0	0	0	0		0
70- < 80	0	0	0	0	0	0	0	0	0	0		0
80- < 90	0	0	0	0	0	0	0	0	0	0		0
90- < 100	0	0	0	0	0	0	0	0	0	0		0
TOTAL	748	245	3	0	0	0	0	0	0	0		996

TABLE 11cd. JOINT DISTRIBUTION OF ACETYLENE AND ETHENE
c. DATA FOR OZONE ABOVE STANDARD, d. DATA FOR HIGH NO (UNREACTED).

C2H2 UG/M3 ** O3 >= 160 UG/M3

C2H4 UG/M3	0 -	10 -	20 -	30 -	40 -	50 -	60 -	70 -	80 -	90 -	100	TOTAL
0- < 10	387	60	1	0	0	0	0	0	0	0		448
10- < 20	2	27	18	2	1	0	0	0	0	0		50
20- < 30	0	0	0	21	0	0	0	0	0	0		21
30- < 40	0	0	0	3	1	0	0	0	0	0		4
40- < 50	0	0	0	0	0	0	0	0	0	0		0
50- < 60	0	0	0	0	0	0	0	0	0	0		0
60- < 70	0	0	0	0	0	0	0	0	0	0		0
70- < 80	0	0	0	0	0	0	0	0	0	0		0
80- < 90	0	0	0	0	0	0	0	0	0	0		0
90- < 100	0	0	0	0	0	0	0	0	0	0		0
TOTAL	389	87	19	26	2	0	0	0	0	0		523

C2H2 UG/M3 ** NO > 60 UG/M3

C2H4 UG/M3	0 -	10 -	20 -	30 -	40 -	50 -	60 -	70 -	80 -	90 -	100	TOTAL
0- < 10	239	5	0	0	0	0	0	0	0	0		244
10- < 20	84	361	9	0	0	0	0	0	0	0		454
20- < 30	0	43	142	16	1	0	0	0	0	0		202
30- < 40	0	0	28	62	6	0	0	0	0	0		96
40- < 50	0	0	0	20	17	1	0	0	0	0		38
50- < 60	0	0	0	0	11	5	0	0	0	0		16
60- < 70	0	0	0	0	0	2	2	1	0	0		5
70- < 80	0	0	0	0	0	0	2	1	0	0		3
80- < 90	0	0	0	0	0	0	0	0	0	0		0
90- < 100	0	0	0	0	0	0	0	0	0	0		0
TOTAL	323	409	179	98	35	8	4	2	0	0		1058

TABLE 12ab. JOINT DISTRIBUTION OF ACETYLENE AND METHANE
a. ALL REDUCED DATA, b. MORNING.

C2H2 UG/M3 **

CH4 UG/M3	0 -	10 -	20 -	30 -	40 -	50 -	60 -	70 -	80 -	90 -	100	TOTAL
700- < 800	263	0	0	0	0	0	0	0	0	0		263
800- < 900	581	1	0	0	0	0	0	0	0	0		582
900- < 1000	533	46	0	0	0	0	0	0	0	0		579
1000- < 1100	401	146	1	0	0	0	0	0	0	0		548
1100- < 1200	642	168	1	0	0	0	0	0	0	0		811
1200- < 1300	205	182	30	2	1	0	0	0	0	0		420
1300- < 1400	46	153	59	5	1	0	0	1	0	0		265
1400- < 1500	10	74	49	24	2	0	0	0	0	0		159
1500- < 1600	8	32	38	35	3	0	0	0	0	0		116
1600- < 1700	2	9	33	30	10	1	0	0	0	0		85
1700- < 1800	4	0	9	14	1	1	1	0	0	0		30
1800- < 1900	1	2	5	14	3	3	1	0	0	0		29
1900- < 2000	1	3	4	8	4	1	0	0	0	0		21
TOTAL	2697	816	229	132	25	6	2	1	0	0		3908

C2H2 UG/M3 ** 0600 - 0900 PST

CH4 UG/M3	0 -	10 -	20 -	30 -	40 -	50 -	60 -	70 -	80 -	90 -	100	TOTAL
700- < 800	17	0	0	0	0	0	0	0	0	0		17
800- < 900	55	0	0	0	0	0	0	0	0	0		55
900- < 1000	69	4	0	0	0	0	0	0	0	0		73
1000- < 1100	33	17	0	0	0	0	0	0	0	0		50
1100- < 1200	68	34	0	0	0	0	0	0	0	0		102
1200- < 1300	48	27	5	1	1	0	0	0	0	0		82
1300- < 1400	8	10	6	2	1	0	0	1	0	0		28
1400- < 1500	0	8	3	1	0	0	0	0	0	0		12
1500- < 1600	1	8	0	1	0	0	0	0	0	0		10
1600- < 1700	1	1	8	1	0	0	0	0	0	0		11
1700- < 1800	0	0	1	0	0	0	0	0	0	0		1
1800- < 1900	0	1	1	5	0	0	0	0	0	0		7
1900- < 2000	0	0	0	1	1	0	0	0	0	0		2
TOTAL	300	110	24	12	3	0	0	1	0	0		450

TABLE 12cd. JOINT DISTRIBUTION OF ACETYLENE AND METHANE
c. EVENING, d. UNREACTED AIR NO >60 ug/m^3.

C2H2 UG/M3 ** 2000 - 2400 PST

CH4 UG/M3	0 -	10 -	20 -	30 -	40 -	50 -	60 -	70 -	80 -	90 -	100	TOTAL
700- < 800	21	0	0	0	0	0	0	0	0	0		21
800- < 900	79	1	0	0	0	0	0	0	0	0		80
900- < 1000	101	21	0	0	0	0	0	0	0	0		122
1000- < 1100	58	56	0	0	0	0	0	0	0	0		114
1100- < 1200	100	31	1	0	0	0	0	0	0	0		132
1200- < 1300	13	37	1	0	0	0	0	0	0	0		51
1300- < 1400	0	37	15	1	0	0	0	0	0	0		53
1400- < 1500	0	5	18	13	1	0	0	0	0	0		37
1500- < 1600	0	1	10	14	1	0	0	0	0	0		26
1600- < 1700	0	0	3	15	8	1	0	0	0	0		27
1700- < 1800	1	0	2	8	1	0	0	0	0	0		12
1800- < 1900	0	0	1	4	2	1	1	0	0	0		9
1900- < 2000	0	0	0	4	1	1	0	0	0	0		6
TOTAL	373	189	51	59	14	3	1	0	0	0		690

C2H2 UG/M3 ** NO >= 60 UG/M3

CH4 UG/M3	0 -	10 -	20 -	30 -	40 -	50 -	60 -	70 -	80 -	90 -	100	TOTAL
700- < 800	4	0	0	0	0	0	0	0	0	0		4
800- < 900	23	1	0	0	0	0	0	0	0	0		24
900- < 1000	52	16	0	0	0	0	0	0	0	0		68
1000- < 1100	34	39	0	0	0	0	0	0	0	0		73
1100- < 1200	113	73	1	0	0	0	0	0	0	0		187
1200- < 1300	33	106	21	2	1	0	0	0	0	0		163
1300- < 1400	9	59	47	5	1	0	0	1	0	0		122
1400- < 1500	3	24	30	17	1	0	0	0	0	0		75
1500- < 1600	1	13	26	18	2	0	0	0	0	0		60
1600- < 1700	0	8	7	17	9	1	0	0	0	0		42
1700- < 1800	0	0	1	5	1	0	1	0	0	0		8
1800- < 1900	0	1	2	8	2	1	1	0	0	0		15
1900- < 2000	0	1	3	7	4	1	0	0	0	0		16
TOTAL	272	341	138	79	21	3	2	1	0	0		657

TABLE 12e. JOINT DISTRIBUTION OF ACETYLENE AND METHANE
e. OZONE ABOVE STANDARD.

	C2H2 UG/M3 ** O3 >= 160 UG/M3										
CH4 UG/M3	0 -	10 -	20 -	30 -	40 -	50 -	60 -	70 -	80 -	90 -	100	TOTAL
700- < 800	55	0	0	0	0	0	0	0	0	0	0	55
800- < 900	135	0	0	0	0	0	0	0	0	0	0	135
900- < 1000	122	0	0	0	0	0	0	0	0	0	0	122
1000- < 1100	51	14	0	0	0	0	0	0	0	0	0	65
1100- < 1200	7	4	0	0	0	0	0	0	0	0	0	11
1200- < 1300	4	9	0	0	0	0	0	0	0	0	0	13
1300- < 1400	1	4	0	0	0	0	0	0	0	0	0	5
1400- < 1500	4	8	3	0	1	0	0	0	0	0	0	16
1500- < 1600	1	10	2	4	0	0	0	0	0	0	0	17
1600- < 1700	1	1	2	4	0	0	0	0	0	0	0	8
1700- < 1800	0	0	0	0	0	0	0	0	0	0	0	0
1800- < 1900	0	0	0	0	0	0	0	0	0	0	0	0
1900- < 2000	0	0	0	0	0	0	0	0	0	0	0	0
TOTAL	381	50	7	8	1	0	0	0	0	0	0	447

TABLE 13ab. JOINT DISTRIBUTION OF ETHANE AND METHANE
a. ALL REDUCED DATA, b. MORNING.

C2H6 UG/M3 **

CH4 UG/M3	0 -	10 -	20 -	30 -	40 -	50 -	60 -	70 -	80 -	90 -	100	TOTAL
700- < 800	270	1	0	0	0	0	0	0	0	0		271
800- < 900	583	2	0	0	0	0	0	0	0	0		585
900- < 1000	340	241	0	0	0	0	0	0	0	0		581
1000- < 1100	231	315	4	0	0	0	0	0	0	0		550
1100- < 1200	616	156	40	0	0	0	0	0	0	0		812
1200- < 1300	99	287	27	6	0	0	0	0	0	0		419
1300- < 1400	7	182	63	12	1	0	0	0	0	0		265
1400- < 1500	2	36	91	14	8	8	1	0	0	0		160
1500- < 1600	5	9	41	35	4	20	1	0	1	0		116
1600- < 1700	1	3	9	39	17	3	13	0	0	0		85
1700- < 1800	3	1	1	3	17	4	1	0	0	0		30
1800- < 1900	1	1	1	3	11	7	5	0	0	0		29
1900- < 2000	1	3	0	3	4	3	7	0	0	0		21
TOTAL	2159	1237	277	115	62	45	28	0	1	0		3924

C2H6 UG/M3 ** 0600 - 0900 PST

CH4 UG/M3	0 -	10 -	20 -	30 -	40 -	50 -	60 -	70 -	80 -	90 -	100	TOTAL
700- < 800	18	0	0	0	0	0	0	0	0	0		18
800- < 900	56	0	0	0	0	0	0	0	0	0		56
900- < 1000	44	30	0	0	0	0	0	0	0	0		74
1000- < 1100	17	32	0	0	0	0	0	0	0	0		49
1100- < 1200	71	20	11	0	0	0	0	0	0	0		102
1200- < 1300	30	38	12	0	0	0	0	0	0	0		80
1300- < 1400	0	22	6	0	0	0	0	0	0	0		28
1400- < 1500	0	5	7	0	0	0	0	0	0	0		12
1500- < 1600	0	2	8	0	0	0	0	0	0	0		10
1600- < 1700	1	0	1	9	0	0	0	0	0	0		11
1700- < 1800	0	0	0	1	0	0	0	0	0	0		1
1800- < 1900	0	0	1	0	6	0	0	0	0	0		7
1900- < 2000	0	0	0	0	2	0	0	0	0	0		2
TOTAL	237	149	46	10	8	0	0	0	0	0		450

TABLE 13c. JOINT DISTRIBUTION OF ETHANE AND METHANE
c. EVENING.

CH4 UG/M3	C2H6 UG/M3 ** 2000 - 2400 PST										
	0 -	10 -	20 -	30 -	40 -	50 -	60 -	70 -	80 -	90 -	100	TOTAL
700- < 800	21	0	0	0	0	0	0	0	0	0		21
800- < 900	78	1	0	0	0	0	0	0	0	0		79
900- < 1000	83	37	0	0	0	0	0	0	0	0		120
1000- < 1100	31	83	0	0	0	0	0	0	0	0		114
1100- < 1200	92	37	3	0	0	0	0	0	0	0		132
1200- < 1300	4	47	0	0	0	0	0	0	0	0		51
1300- < 1400	0	24	28	1	0	0	0	0	0	0		53
1400- < 1500	0	1	22	4	5	5	0	0	0	0		37
1500- < 1600	0	0	5	9	2	9	0	0	1	0		26
1600- < 1700	0	1	0	7	10	0	9	0	0	0		27
1700- < 1800	1	0	0	0	8	2	1	0	0	0		12
1800- < 1900	0	0	0	1	0	5	3	0	0	0		9
1900- < 2000	0	0	0	0	1	1	4	0	0	0		6
TOTAL	310	231	58	22	26	22	17	0	1	0		667

TABLE 14. JOINT DISTRIBUTION OF OZONE AND OXIDANT.

Ox UG/M3	O3 UG/M3 ** 0 -	50 -	100 -	150 -	200 -	250 -	300 -	350 -	400 -	450 -	500	TOTAL
0- < 50	2438	188	0	0	0	0	0	0	0	0		2626
50- < 100	49	428	51	0	0	0	0	0	0	0		528
100- < 150	0	21	275	40	2	0	0	0	0	0		338
150- < 200	0	0	22	159	73	3	0	0	0	0		257
200- < 250	0	0	0	8	105	66	2	0	0	0		181
250- < 300	0	0	0	0	4	67	22	5	0	0		98
300- < 350	0	0	0	0	0	4	30	26	4	0		64
350- < 400	0	0	0	0	0	0	3	15	12	0		30
400- < 450	0	0	0	0	0	0	0	0	6	0		6
450- < 500	0	0	0	0	0	0	0	0	0	1		1
TOTAL	2487	637	348	207	184	140	57	46	22	1		4129

TABLE 15a. JOINT DISTRIBUTION OF OZONE AND NO_x
a. ALL REDUCED DATA

NOX UG/M3	O3 UG/M3 ** 0 -	50 -	100 -	150 -	200 -	250 -	300 -	350 -	400 -	450 -	500	TOTAL
0- < 50	280	190	87	49	26	3	0	0	0	0		635
50- < 100	588	271	220	87	107	90	34	21	10	0		1428
100- < 150	699	135	49	43	27	28	21	19	9	1		1031
150- < 200	527	67	29	19	18	16	2	3	2	0		683
200- < 250	406	35	12	7	5	2	0	0	1	0		468
250- < 300	269	29	2	1	0	1	0	1	0	0		303
300- < 350	170	17	5	4	1	0	0	0	0	0		197
350- < 400	92	7	1	0	0	0	0	1	0	0		101
400- < 450	76	3	0	0	0	0	0	1	0	0		80
450- < 500	47	1	0	0	0	0	0	0	0	0		48
500- < 550	47	0	0	0	0	0	0	0	0	0		47
550- < 600	27	0	0	0	0	0	0	0	0	0		27
600- < 650	13	0	0	0	0	0	0	0	0	0		13
650- < 700	9	0	0	0	0	0	0	0	0	0		9
700- < 750	11	0	0	0	0	0	0	0	0	0		11
750- < 800	2	0	0	0	0	0	0	0	0	0		2
800- < 850	3	0	0	0	0	0	0	0	0	0		3
850- < 900	2	1	0	0	0	0	0	0	0	0		3
900- < 950	1	2	0	0	0	0	0	0	0	0		3
950- < 1000	0	0	0	0	0	0	0	0	0	0		0
TOTAL	3269	758	405	210	184	140	57	46	22	1		5092

TABLE 15b. JOINT DISTRIBUTION OF OZONE AND NO_x
b. NMEO ABOVE STANDARD

	O3 UG/M3 ** C2H4+C2H2+C3+ > 160 UG/M3										
NOX UG/M3	0 -	50 -	100 -	150 -	200 -	250 -	300 -	350 -	400 -	450 -	500	TOTAL
0- < 50	18	17	12	23	9	2	0	0	0	0		81
50- < 100	258	146	126	54	64	57	24	20	8	0		757
100- < 150	561	120	40	29	22	21	19	14	8	1		835
150- < 200	454	65	25	18	18	14	2	3	2	0		601
200- < 250	354	32	11	7	5	1	0	0	1	0		411
250- < 300	245	26	2	0	0	1	0	0	0	0		274
300- < 350	153	16	5	4	1	0	0	0	0	0		179
350- < 400	87	7	1	0	0	0	0	1	0	0		96
400- < 450	72	3	0	0	0	0	0	1	0	0		76
450- < 500	44	1	0	0	0	0	0	0	0	0		45
500- < 550	44	0	0	0	0	0	0	0	0	0		44
550- < 600	27	0	0	0	0	0	0	0	0	0		27
600- < 650	12	0	0	0	0	0	0	0	0	0		12
650- < 700	9	0	0	0	0	0	0	0	0	0		9
700- < 750	11	0	0	0	0	0	0	0	0	0		11
750- < 800	2	0	0	0	0	0	0	0	0	0		2
800- < 850	3	0	0	0	0	0	0	0	0	0		3
850- < 900	2	1	0	0	0	0	0	0	0	0		3
900- < 950	1	2	0	0	0	0	0	0	0	0		3
950- < 1000	0	0	0	0	0	0	0	0	0	0		0
TOTAL	2357	436	222	135	119	96	45	39	19	1		3469

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APPENDIX

Back Extrapolation

An obvious criticism of the direct correlation of oxidant/ozone with NMHC/NOx in the same sample is that the same chemistry which produces ozone will destroy NMHC and perhaps NOx. This argument might also explain any discrepancy between ambient data and inventory data. This project offered means to verify and allow for this because it provides two independent measures of degree of reaction and clearly indicates samples which have undergone little or no reaction.

1) Since ethene and acetylene are derived almost exclusively from car exhaust they must enter the atmosphere (unless the air sample inadvertently comes mainly from one atypical vehicle) in a consistent ratio. Ethene is several times more reactive than acetylene so extensively reacted mixtures show a significant decrease in the ethene/acetylene ratio.

2) Combustion sources produce NO predominently which is converted by atmospheric chemistry to NO_2. There is neither experimental nor theoretical reason to believe that NO is ever reformed by any process in the real atmosphere even though "pure" NO_2 can be photolyzed to NO in laboratory systems.

Assume that the relative/fractional rates of disappearance of individual hydrocarbons are always the same and independent of degree of reaction, brightness of sunlight and other factors. This can be symbolized by a free radical concentration [R] which might be thought of as OH although the following derivation is not dependent on the assumption that OH is actually that attacking species.

$HC_i + R$ loss of hydrocarbon k_i

$$\frac{d \ln[C_i]}{dt} = -k_i[R]$$

when $[C_i]$ = concentration of hydrocarbon i

k_i = rate constant for hydrocarbon i reaction with R

$[R^\cdot]$ = concentration of attacting free radical

$[C_{io}]$ = Initial concentration of hydrocarbon i

$$[C_{io}] = [C_i] \exp k_i \int_o^t [R]\, dt \qquad (1)$$

If this is applied to ethene ($[C_{Et,o}] \rightarrow [C_{Et}]$)

and acetylene ($[C_{ac,o}] \rightarrow [C_{ac}]$)

the integral can be evaluated

$$\int_o^t [R]\, dt = [k_{Et} - k_{ac}]^{-1} \ln[C_{Eto}]\ [C_{ac}]\ [C_{ac,o}]^{-1}\ [C_{Et}]^{-1}$$

If (1) is summed over all hydrocarbons

$$\Sigma[C_{io}] = \Sigma[C_i] \exp k_i \int_o^t [R]\, dt = \Sigma[C_i]\ \Sigma f_i \exp k_i \int_o^t [R]\, dt$$

In which $f_i = [C_i]/\Sigma[C_i]$ represents the fraction of the hydrocarbon which has reactivity k_i. These fractions refer to the hydrocarbons composition in the reacted state as measured. In the most reacted samples the ethene was reduced to about half of the acetylene value. Using rate constants for the reaction of OH with ethene (3.8×10^9 ℓ $mole^{-1}$ sec^{-1}) and acetylene, (0.11×10^9 ℓ $mole^{-1}$ sec^{-1}) we can estimate the value of the integral:

$$\int_o^t [R]dt = \frac{\ln 2}{3.7 \times 10^9} = 1.9 \times 10^{-10} \quad \text{ℓ mole}^{-1}\ \text{sec}^{-1}$$

*K. R. Darnall, A. C. Lloyd, A. M. Winer and James N. Pitts, Jr.
Env. Sci. and Tech. 10, p. 692, July 1976

To estimate the "depletion factor"

$$\Sigma f_i \exp k_i \int_o^t [R]\,dt$$

an estimate of hydrocarbon distribution, f_i, with reactivity k_i is needed. A simplifying assumption is that the highly reactive olefins are completely reacted but present in small quantitites to begin with so they are ignored. The remainder may be split 2/3 paraffins of OH reactivity equal to ethene and 1/3 aromatics with twice the reactivity of ethene then the depletion factor will be nearly three. The joint distribution tables 8a,b,c do not suggest a loss of higher hydrocarbons of this magnitude.

It also was assumed that the atmosphere operated as a batch reactor. Since additions of organics continue during daylight hours a stirred flow reactor equation would be more appropriate. This probably would make little difference as long as the ethene/acetylene ratio is used as the measure of degree of reaction and the assumption is made that the bulk of the higher hydrocarbon has a reactivity not differing greatly from ethene.